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THE VAPOR PRESSURE OF METALLIC TUNGSTEN.[1]

By Irving Langmuir.

THE vapor pressure of metals has been the subject of many investigations in recent years.

Greenwood[2] has directly determined the boiling points of several metals at three or four different pressures. The method adopted was to heat the metal in a carbon or magnesia crucible in an electric furnace and to observe the temperature at which drops of metal were first thrown up from the molten surface. The metals studied were copper, tin, silver, lead, bismuth, antimony, magnesium, iron, chromium, manganese, and aluminum. The boiling points at atmospheric pressure ranged from 1120° C. for magnesium to 2450° for iron.

Recently von Wartenburg[3] has determined quantitatively the vapor pressures of lead, silver, and thallium by the dynamical method, that is, by passing an inert gas very slowly over the heated metal and measuring the concentration of the metal vapor in the gas.

The volatility of many metals has been qualitatively observed, but except in the case of the metals given above and such easily volatile metals as mercury, zinc, and the alkali and alkaline earth metals there are no quantitative determinations of the vapor pressures or boiling points known to the writer.

The volatility of the materials used for filaments of incandescent lamps is the principal factor determining the useful life of such lamps.

Experiments were therefore undertaken to determine the rate of evaporation of tungsten in vacuum at various temperatures up to the melting point.

The kinetic theory enables us to calculate the vapor pressure from this

[1] A preliminary statement of the results of this investigation has appeared in the Journal of the Amer. Chem. Soc., *35*, 931, 1913.

[2] Chem. News, *104*, 31–33, 42–45, 1912.

[3] Z. f. Electrochem., *19*, 482, 1913.

rate of evaporation, or at least to obtain a lower limit for the vapor pressure.

RELATION BETWEEN VAPOR PRESSURE AND RATE OF EVAPORATION IN A VACUUM.

Let us consider a surface of metal in equilibrium with its saturated vapor. According to the kinetic theory we look upon the equilibrium as a balance between the rate of evaporation and the rate of condensation. That is, we conceive of these two processes going on simultaneously at equal rates.

In the case of liquids or solids at temperatures near their boiling points or even at temperatures so low that their vapor pressures are in the neighborhood of one millimeter, we are accustomed to consider that there must always be equilibrium between the vapor and the liquid or solid at the surface between the two. For example, no matter how rapidly we may boil water we are probably justified in considering that the steam is saturated at the surface boundary between the water and the steam.

This, however, simply means that when we boil water as rapidly as we can, the net rate at which steam is produced is very small compared to the actual rate at which the water is evaporating into steam and the steam again condensing on the water.

At much lower temperatures, where the vapor pressure is of the order of magnitude of .001 mm. the rate of evaporation of a substance even in a practically perfect vacuum is very small. This is not due to the cooling of the substance by its own evaporation, but simply to the fact that the rate at which the molecules of vapor are formed is limited.

For example, we cannot make mercury freeze by placing it in a very high vacuum, although we know it has a perceptible vapor pressure even at its freezing point.

At temperatures so low that the vapor pressure of a substance does not exceed a millimeter, we may consider that the actual rate of evaporation of a substance is independent of the presence of vapor around it. That is, the rate of evaporation in a high vacuum is the same as the rate of evaporation in presence of saturated vapor. Similarly we may consider that the rate of condensation is determined only by the pressure of the vapor.

Now the rate at which the saturated vapor comes into contact with the metal may be readily calculated from the principles of the kinetic theory when the vapor pressure is known. Certainly the rate of condensation of the vapor cannot exceed the rate with which it comes into contact with the solid or liquid.

This calculation is similar to that of the effusion of gases through small openings.[1]

Let us consider a unit cube of the vapor one side of which is bounded by the metal. We will calculate the rate at which the vapor comes into contact with the metal. Half of the molecules in this unit volume are moving towards the metal, and the other half are moving away from it. If we let ρ be the density of the gas, then the mass of gas moving toward the metal is $\frac{1}{2}\rho$.

Let Ω be the average (arithmetical) velocity of the molecules. It can be readily shown that the average *component* of the velocity in any given direction is then $\frac{1}{2}\Omega$. Hence the average velocity with which the gas molecules in the mass $\frac{1}{2}\rho$ are *approaching* the metal is $\frac{1}{2}\Omega$. The mass of gas (m) which strikes against the unit surface of metal per second is therefore $\frac{1}{2}\rho \times \frac{1}{2}\Omega$, thus

$$m = \tfrac{1}{4}\rho\Omega. \tag{1}$$

The ordinary gas law $pV = RT$ may be written

$$\rho = \frac{pM}{RT}, \tag{2}$$

where p = pressure,
M = molecular weight,
T = absolute temperature (° Kelvin),
R = gas constant = 83.2×10^6 ergs per degree.

The average velocity (Ω) of the molecules is given by the relation

$$p = \frac{\pi}{8}\rho\Omega^2, \tag{3}$$

whence from (2)

$$\Omega = \sqrt{\frac{8RT}{\pi M}}. \tag{4}$$

Substituting (2) and (4) in (1) we get for the rate at which the vapor comes into contact with the metal

$$m = \sqrt{\frac{M}{2\pi RT}} \cdot p. \tag{5}$$[2]

If we can assume that every atom of the vapor which strikes the metal condenses, then the equation (5) gives the desired relation between the vapor pressure and the rate of evaporation in vacuo. If, however, a certain proportion (r) of the atoms of the vapor is reflected from the surface then the vapor pressure will be greater than that calculated from (5) in the ratio $1 : (1 - r)$.

[1] Cf. Meyer's Kinetic Theory of Gas, German edition, 1899, p. 82.

[2] This equation has been previously used by the author in calculating the velocity of reaction between oxygen and tungsten. Jour. Amer. Chem. Soc., *35*, 106, 1912.

There are good reasons for believing that the reflection of vapor molecules from the surface takes place to a negligible degree only. Knudsen[1] has shown from measurements of the heat conductivity of gases at low pressures that the number of molecules of a gas which are reflected from a smooth surface (*i. e.*, do not reach thermal equilibrium with the surface) is as much as 70 per cent. in the case of hydrogen but very much less with gases of higher molecular weight. Knudsen gives the name accommodation coefficient to the quantity $1 - r$. He finds for example

Gas.	Surface.	Accommodation Coefficient.
H_2	Polished platinum	0.36
CO_2	Polished platinum	0.87
H_2	Platinized platinum	0.71
CO_2	Platinized platinum	0.98

Timiriazeff[2] finds the accommodation coefficient to have significance in determining the "slip" of gases in viscosity measurements at low pressure.

The accommodation coefficient for a vapor, with such high molecular weight as that of tungsten would probably be nearly unity for any kind of surface. There is every reason to believe, moreover, that the accommodation coefficient would be particularly high in the case of a metal and its own saturated vapor. It is extremely probable therefore that equation (5) gives a very close approximation to the true vapor pressure.

Knudsen[3] has determined the vapor pressure of mercury at temperatures from 0° to 50° by a method involving the use of an equation similar to (5). He used a relatively large surface of mercury, however, and allowed the saturated vapor thus obtained to escape through a small opening into a space practically free from mercury vapor. From the rate of escape of the mercury he calculated the pressure of the vapor by an equation equivalent to (5). This method differs in principle from that employed for the present determination of the vapor pressure of tungsten only in having an opening through which the vapor diffuses instead of having the vapor simply diffuse out through the surface of the metal itself. Knudsen's method has the advantage that his results are practically unaffected by any possible reflection of the vapor molecules from the surface, but it has the disadvantage that is cannot be directly applied to determining the vapor pressures of such difficultly volatile substances as tungsten.

[1] Ann. Phys., *34*, 593, 1911.
[2] Ann. Phys., *40*, 971, 1913.
[3] Ann. Physik., *29*, 179, 1909.

VARIATION OF THE RATE OF EVAPORATION WITH THE TEMPERATURE.

The relation between the vapor pressure of any substance and the temperature is given by the Clausius-Clapeyron formula.

$$\lambda = T\frac{dp}{dT}(v - v_0). \tag{6}$$

In the case of tungsten the volume of the metal is entirely negligible as compared to the volume of the vapor, so we may place $v_0 = 0$. If we consider λ to be the latent heat of evaporation per mol of tungsten (184 grams) then since $pv = RT$ we have

$$\frac{d\ln p}{dT} = \frac{\lambda}{RT^2}. \tag{7}$$

This result could have been obtained directly from Van't Hoff's equation.

In general λ is a function of the temperature such that

$$\frac{d\lambda}{dT} = C_v - C_s, \tag{8}$$

here C_v is the specific heat (per mol) of the vapor (at constant pressure), and C_s is the specific heat per mol of the solid metal.

We may safely consider tungsten vapor to be monatomic[1] and hence its specific heat at constant pressure is

$$C_v = 2.98 + R = 4.96 \text{ calories per gram atom.} \tag{9}$$

The atomic heat of solid tungsten is given as 6.3 by Gin (1908) and as 7.8 by Corbino.[2] The higher value is rather improbable, so that the best value would seem to be about

$$C_s = 6.8. \tag{10}$$

Substituting (9) and (10) in (8) and integrating we have:

$$\lambda = \lambda_0 - 1.8T. \tag{11}$$

This result substituted in (7) and integrated gives, after changing from natural to common logarithms:

$$\log p = A - \frac{0.218\lambda_0}{T} - 0.9 \log T, \tag{12}$$

where A is a constant of integration.

Taking the logarithm of equation (5) we obtain

$$\log m = \log p + \tfrac{1}{2} \log \frac{M}{2\pi R} - \tfrac{1}{2} \log T. \tag{13}$$

Combining this with (12):

[1] Langmuir, Jour. Amer. Chem. Soc., *35*, 944, 1913.

[2] Phys. Zeitsch., *13*, 375, 1912.

$$\log m = A' - \frac{0.218\lambda_0}{T} - 1.4 \log T, \tag{14}$$

where

$$A' = A + \tfrac{1}{2} \log \frac{M}{2\pi R}. \tag{15}$$

Equation (14) gives us the rate of evaporation of tungsten as a function of the temperature. There are two empirical constants A' and λ_0 to be determined from the experiments.

EXPERIMENTS ON THE RATE OF EVAPORATION OF TUNGSTEN IN VACUUM.

Several sets of experiments were made to determine the rate of evaporation. In each case lamps were made up with tungsten filaments, and the filaments were heated for various times at various temperatures. The rate of evaporation was determined usually by both of two methods, namely by increase in resistance and by decrease in weight.

First Set.—Five tungsten lamps were made up with single loop filaments without supports. The length of the wire used ranged from 10.6 to 11.2 cm. and the diameter was .0162 cm. These lamps were set up on life test at an efficiency of one watt per maximum horizontal candle power and maintained at constant voltage. The initial candle power varied from 40 to 41 among the various lamps. These lamps were taken off test after 500 to 1,000 hours, broken open, and the filaments weighed.

Second Set.—Five lamps similar to the last with lengths of filament from 10.6 to 11.2, and of the same diameter as before were set up on test at 0.8 watt per maximum horizontal candle power and maintained at constant voltage. The initial candle powers ranged from 58.5 to 60.5. These lamps were taken off test after 200 to 300 hours, and the filaments were weighed.

Third Set.—Two lamps containing single loop filaments of wire .0122 cm. diam. were made up. The filament of the first was 11.1 cm. long. This lamp was set up at constant voltage at an original temperature of 2800° K. (determined by color). The readings taken at frequent intervals were:

TABLE I.

Time, Minutes.	Volts.	Amperes.	Candle Power.
0	23.6	2.94	164
14	23.6	2.93	—
21	23.6	2.93	153
56	23.6	2.89	124
72	23.6	2.88	112

The second lamp had a filament 14.3 cm. long. This lamp was set

up by color at 3136° K. and kept at constant voltage. The characteristics were:

TABLE II.

Time, Minutes.	Volts.	Amperes.	Candle Power.
0	35.5	3.55	504
1	35.5	——	311
2	35.5	3.38	238
3	35.5	3.30	199

Fourth Set.—This set was made up at a later date than the previous ones, and the measurements were conducted with much greater care. Five lamps were made up from wire .00709 cm. diameter, each with a length of about 77 cm. mounted in six loops. These lamps were photometered and set up with the filaments at temperatures ranging from 2738 to 2925° K.

The voltage was adjusted at frequent intervals so as to keep the product $V\sqrt[3]{A}$ constant. (V = volts, A = amperes.) In this way, notwithstanding a considerable change in the diameter of the filament, the temperature is maintained constant. This is readily seen from the following reasoning. The energy radiated is proportional to the diameter whence the function VA/d (watts divided by the diameter) is a function of the temperature but not of the diameter. Similarly if the material of the wire is unaltered, the resistance is inversely proportional to the square of the diameter, hence Vd^2/A is a function of the temperature but not of the diameter. Therefore

$$\frac{V^2A^2}{d^2} \times \frac{Vd^2}{A} = V^3A$$

is a function of the temperature but not of the diameter. Hence if $V\sqrt[3]{A}$ is maintained constant the temperature must remain constant even when the diameter changes.

The weight of the wire before sealing into the lamps was found to be 0.764 mg. per cm. of length.

The lamps were run as follows:

TABLE III.

No.	Temp.	Initial Volts.	Initial Amps.	Time, Minutes.	Final Volts.	Final Amps.	Final Wt. Mg per Cm.
1	2738	195	1.182	233	198	1.129	
2	2825	208	1.240	111	213	1.157	0.676
3	2875	216	1.260	65	222	1.159	0.671
4	2925	230	1.310	40	238	1.184	0.656
5	2930	235	1.318	14.5	237	1.269	0.722

The temperatures were determined by comparison of the color of the light emitted from the filament with that of a standard lamp viewed through a special blue glass. The details of this method of estimating temperatures will be given in a subsequent paper. For the present it will suffice to say that the temperature scale is primarily based on the following formula

$$T = \frac{11{,}230}{7.029 - \log H}. \tag{16}$$

Here H is the intrinsic brilliancy of the filament in international candle power per sq. cm. (projected area). On this scale the melting point of tungsten is 3540° K.

The initial volts and amperes give the characteristics of the lamps as first set up (after two hours ageing of the filament at 2400° K.).

The final volts and amperes give the characteristics after being set up at the indicated temperature for the time given in the fourth column.

The final weight is the average weight per unit length as found by weighing several lengths of the filament on a delicate microbalance after breaking open the bulbs.

CALCULATION OF THE RATE OF EVAPORATION.

Let w_0 = the original weight of the wire per unit length,
w = the weight per unit length after the time t,
ρ = the density of the wire,
r = radius of the wire,
R_0 = its initial resistance per unit length,
R = its final resistance per unit length.

Then it is easily seen that

$$w = \pi r^2 \rho,$$

or

$$r = \sqrt{\frac{w}{\pi\rho}}. \tag{17}$$

Now the effect of the evaporation is to remove tungsten from the surface at a rate proportional to the extent of the surface. That is, the thickness removed per unit time is constant and equal to m/ρ. Therefore

$$\frac{m}{\rho} = \frac{r_0 - r}{t} = \frac{\sqrt{w_0} - \sqrt{w}}{t} \frac{1}{\sqrt{\pi\rho}}, \tag{18}$$

whence

$$m = \sqrt{\frac{\rho}{\pi}} \cdot \frac{\sqrt{w_0} - \sqrt{w}}{t}. \tag{19}$$

This equation gives the rate of evaporation m in terms of the density and weight per unit of length of the filament.

Since the resistance is inversely proportional to the cross-section we have

$$\frac{R_0}{R} = \frac{w}{w_0}. \tag{20}$$

Substituting this in (19) gives

$$m = \sqrt{\frac{\rho}{\pi}}\sqrt{w_0} \cdot \frac{1 - \sqrt{\frac{R_0}{R}}}{t}, \tag{21}$$

from which m can be calculated from the changes in resistance.

It should be noted, however, that (20) assumes that the specific resistance remains unaltered, therefore equation (21) applies only when the filament is kept at constant temperature, as for example in the fourth set of experiments. In the first three sets of experiments, on the other hand, the lamps were run at constant voltage. The temperature therefore gradually decreases, and for this reason the resistance does not increase as rapidly as if the filament were kept at constant temperature. From data on the characteristics of tungsten filaments available in this laboratory it has been calculated that at constant voltage a 1 per cent. decrease in current corresponds to a decrease in cross-section of 1.11 per cent. or an increase of 1.11 per cent. in resistance at constant temperature. Therefore, before applying equation (21) to the data in the first three sets of experiments an 11 per cent. correction should be made in the changes in the resistance that are produced by the evaporation.

In calculating m from equations (19) or (21) the value of ρ was taken to be 19.4 which gives for $\sqrt{\rho/\pi}$ the value 2.486 in gram cm. units.

In calculating the values of m from the data of the fourth set of experiments, the values of $\sqrt{R_0/R}$ were plotted as a function of t and the best representative straight line was drawn among them. The slope of this line was used to calculate m according to equation (21).

Results of Experiments.

The values of m, *i. e.*, the rate of evaporation of tungsten in grams per sq. cm. per second, were calculated by equations (19) and (21) as described above, and are tabulated below (Table IV.).

In order to determine whether m, the rate of evaporation, varies with the temperature according to the theoretical equation (14) the quantity $\log m + 1.4 \log T$ (column VI.) was plotted (Fig. 1) against $1/T$ (column V.).

According to equation (14) the points should lie along a straight line. Reference to Fig. 1 will show that the agreement is excellent, although the values of m vary in the ratio 1 : 15,000.

TABLE IV.

I. Set.	II. Lamp.	III. Temp. of Fil. °K.	IV. $m \times 10^6$.	V. $\frac{1}{T} \times 10^6$.	VI. $\log m + 14 \log T$.	VII. Method.
I.	—	2440	0.0020	409.8	6.05–10	Weight.
II.	—	2522	0.0059	396.5	6.53–10	"
III.	1	2800	0.39	357.1	8.42–10	Resistance.
"	2	3136	30.	318.9	0.38—	"
IV.	1	2738	0.151	365.2	7.99–10	"
"	2	2825	0.52	354.0	8.54–10	"
"	2	2825	0.59	354.0	8.59–10	Weight.
"	3	2875	1.01	347.8	8.84–10	Resistance.
"	3	2875	1.14	347.8	8.90–10	Weight.
"	4	2925	1.73	341.9	9.10–10	Resistance.
"	4	2925	2.33	341.9	9.23–10	Weight.
"	5	2930	1.84	341.3	9.13–10	Resistance.
"	5	2930	2.45	341.3	9.25–10	Weight.

The values of m determined by the change in resistance are in every case lower than those found from the change in weight. This is due to the fact that the elimination of traces of impurities from the tungsten by volatilization and a slow sintering process tend to decrease the specific resistance of the tungsten and hence counteract the increase in resistance due to evaporation. In fact, in the first and second sets of experiments at 2440 and 2520° respectively, the resistance during the first part of the life actually *decreased*, so that the resistance measurements are totally unreliable as a source of information about the rate of evaporation. At higher temperatures, however, these changes in specific resistance take place much more rapidly than at lower temperatures, and the resistance measurements become of greater significance.

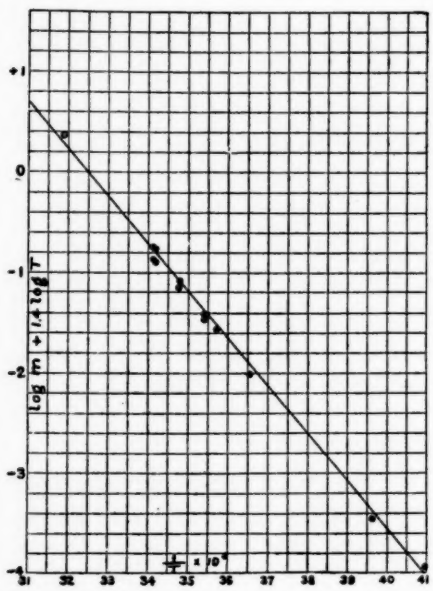

Fig. 1.

The values of m found from the changes in resistance are therefore probably not as accurate as those found from the loss of weight, but nevertheless serve as a very valuable check on the latter.

From the slope of the straight line in Fig. 1 we obtain

$$0.218\lambda_0 = 47{,}440,$$

whence

$$\lambda_0 = 217{,}800 \cdot g\text{—calories per mol.}$$

From this by (11) the heat of evaporation of tungsten at any temperature is $\lambda = 217{,}800 - 1.8T$.

We can also calculate the value of A', equation (14), from Fig. 1. We obtain

$$A' = 15.402.$$

Equation (14) thus becomes

$$\log m = 15.402 - \frac{47{,}440}{T} - 1.4 \log T. \tag{22}$$

From (15) we can now calculate A; equation (12) thus becomes

$$\log p = 15.502 - \frac{47{,}440}{T} - 0.9 \log T. \tag{23}$$

Since equation (22) represents the straight line on Fig. 1, it is readily seen that this equation gives a very satisfactory method of calculating the rate of evaporation at any temperature.

Similarly, if we may assume that the reflection of tungsten atoms from solid tungsten is small, then equation (23) must give the vapor pressure with a fair degree of accuracy.

In Table V. are given the rate of evaporation, and the vapor pressure of tungsten at various temperatures as calculated from equations (22)

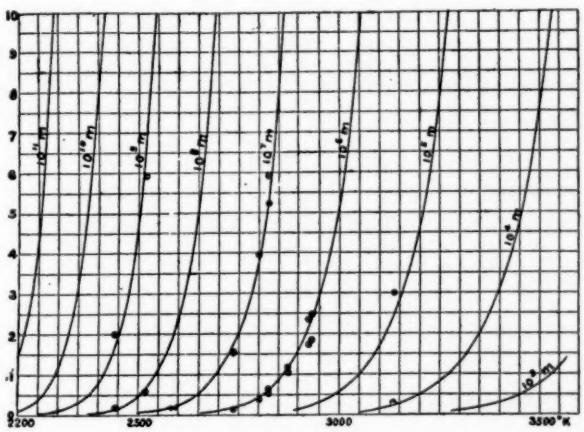

Fig. 2.

Rate of evaporation of tungsten in a vacuum (m = grams of tungsten per square cm. per sec.). Points experimentally determined (see Table IV.); curves calculated from equation (22).

TABLE

Rate of Evaporation and Vapor Pressure of Tungsten.

Absolute Temp.	Evaporation g per sq. cm. per sec.	Vapor Pressure, mm.
2000° K.	$114. \times 10^{-15}$	6.45×10^{-12}
2100	1.44×10^{-12}	83.2×10^{-12}
2200	14.4×10^{-12}	$849. \times 10^{-12}$
2300	116.7×10^{-12}	7.05×10^{-9}
2400	$798. \times 10^{-12}$	49.2×10^{-9}
2500	4.67×10^{-9}	$294. \times 10^{-9}$
2600	23.6×10^{-9}	1.51×10^{-6}
2700	$106. \times 10^{-9}$	6.95×10^{-6}
2800	$429. \times 10^{-9}$	28.6×10^{-6}
2900	1.57×10^{-6}	$106. \times 10^{-6}$
3000	5.23×10^{-6}	0.000362
3100	16.3×10^{-6}	0.00114
3200	46.7×10^{-6}	0.00333
3300	$126. \times 10^{-6}$	0.00910
3400	$320. \times 10^{-6}$	0.0234
3500	$769. \times 10^{-6}$	0.0572
(3540)	.00107	0.080
(5110)	——	760.

and (23). Above the melting point of tungsten the vapor pressure would follow another curve. The boiling point 5110° calculated from equation (23) must therefore be looked upon as a lower limit. However, since the heat of fusion of metals is very small compared to their heats of vaporization the error is certainly not large, and it can therefore be safely concluded that the boiling point of tungsten must lie in the neighborhood of 5100° K.

The data in Table V. have been plotted in Figs. 2 and 3. In Fig. 2 the rates of evaporation as determined by experiment (Table IV.) are plotted. It is seen that the equation (22) fits in well with the observations.

SUMMARY.

1. It is shown that the vapor pressure (p) of a substance is related to its rate of evaporation (m) in a vacuum by the following relation:

$$m = \sqrt{\frac{M}{2\pi RT}}\, p,$$

where M is the molecular weight of the vapor. In the derivation of this equation it is assumed that all the molecules of vapor which strike the surface of the metal are condensed (not reflected). No other assumptions except those that have received ample experimental verification need be made.

2. Experiments were made to determine the rate of evaporation of tungsten in a vacuum at temperatures ranging from 2440° K. up to 3136° K. Over this temperature interval of 700° the rate of evaporation increased in the ratio 1 : 15,000.

3. From these data the vapor pressures were calculated and were found to agree excellently with the thermodynamical relations such as the Clausius-Clapeyron formula. The latent heat of evaporation of solid tungsten is thus found to be (per 184 grams)

$$\lambda = 217{,}800 - 1.8T \text{ calories},$$

a value higher than the heat evolved by any known chemical reaction.

4. The rate of evaporation of tungsten at any temperature in a perfect vacuum is given accurately by the equation

$$\log_{10} m = 15.402 - \frac{47{,}440}{T} - 1.4 \log_{10} T;$$

here m is the rate of evaporation in grams per sq. cm. per second.

5. The vapor pressure of tungsten in mm. of mercury at the absolute temperature T is given by the equation

$$\log_{10} p = 15.502 - \frac{47{,}440}{T} - 0.9 \log_{10} T.$$

6. The vapor pressure of tungsten at 2400° K. the temperature of the filament in a lamp running at 1 watt per candle, is about 50×10^{-9} mm.

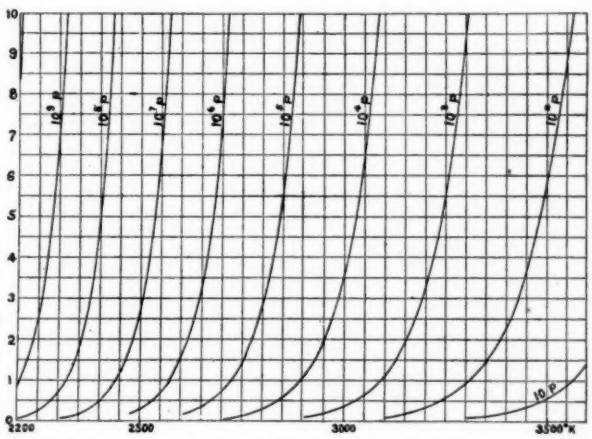

Fig. 3.

Vapor pressure of tungsten in millimeters of mercury.

At the melting point of tungsten, 3540° K., the vapor pressure is 0.080 mm. The boiling point of tungsten at atmospheric pressure is probably very

close to 5100° K. The vapor pressure at other temperatures is given in Table V.

7. The rate of evaporation and the vapor pressure of tungsten are given in Table V. Curves of the same data are given in Figs. 2 and 3.

In subsequent papers the writer intends to publish data on the rates of evaporation and vapor pressures of platinum, carbon, molybdenum, tantallum, osmium, and some of the commoner metals such as copper, silver, nickel, and iron.

RESEARCH LABORATORY,
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THE INFRA-RED OPTICAL PROPERTIES OF SOME SULPHIDES: A BALANCED METHOD OF USING THE BOLOMETER.

BY IRVING B. CRANDALL.

THE relation between the optical properties of compounds and their chemical properties has been investigated for a number of substances in the visible and ultra-violet regions of the spectrum. Certain organic compounds have also been experimented with in the infra-red spectrum in a systematic manner, but little has been done in this region with classes of inorganic compounds (including minerals) if we except the work of Nichols and his students on the reflection from salts of the alkaline earths,[1] of Clark on the reflection from chromates,[2] of Morse on the reflection from carbonates,[3] of Rub[illegible] Hollnagel on the reststrahlen from salts of the alkalies,[4] and of Coblentz on the rôle of water in minerals.[5] Perhaps the field seems unpromising on account of the difficulty of obtaining good pieces of the right dimensions of the solids in question, and polishing their surfaces.

Last year Prof. A. Trowbridge, noting the perfect cleavage in one direction of the minerals molybdenite and stibnite, was led to investigate the optical properties of thin layers of these substances. He used an infra-red spectrograph of moderate resolving power, and obtained approximate values for the extinction modulus $n\chi$ for the two substances. On observing the transmission of very thin cleavage layers of molybdenite there were found broad absorption bands, regularly spaced, beginning at wave-length 5 or 6μ. The same piece exhibited bands close together in the very short region in the red end of the visible spectrum for which it was transparent. It was not known whether these bands were due to interference in the layer, or simply to ordinary absorption. The object of undertaking the present investigation was to repeat these measurements with apparatus of larger resolving power, and determine, if possible, the refractive indices. In addition, it was planned to experiment with other sulphides, and discover any common optical properties

[1] PHYS. REV., XXVII., 1908, p. 225, and other papers.
[2] Astro. Jour., 35, 1912, p. 48.
[3] Astro. Jour., 26, 1907, p. 225.
[4] Sitz. Ber. Preus. Akad. Wiss., Berlin, 4, 1910, p. 26.
[5] Jour. Fr. Inst., CLXXII., 1911, p. 309.

that might exist. The position and magnitude of the bands shown by molybdenite were to receive especial consideration, as, if they proved to be due to interference, a way might be found to determine the refractive index that did not depend on the reflecting power. The refractive indices of molybdenite and stibnite were known to be very high[1] so that they should be interesting substances from this point of view alone. Before going further, we may remark that the sulphides are, next to the halogen salts and oxides, the simplest class of binary metallic compounds, and ought to give easily interpreted results.[2]

A Balanced Method of Using the Bolometer.

In the work to be hereinafter described the bolometer was used in a manner perhaps unusual, for comparing intensities of radiation in the infra-red spectrum; we therefore proceed to consider the method somewhat in detail.

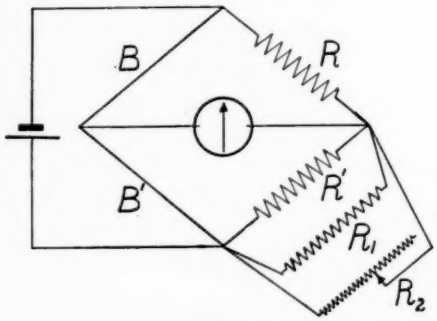

Fig. 1.

A linear bolometer of the usual form was constructed, the dimensions of the two strips forming two arms of the Wheatstone bridge being in width 0.5 mm. and in length 25 mm. These had a resistance of about 4 ohms each. The other two arms of the bridge were coils of manganin wire situated within the bolometer case, and having a resistance of 20 ohms each. The connections are as given in Fig. 1. A current of about 0.08 ampere traversed each arm of the bridge. The radiation is supposed to fall on the strip *B*.

[1] See later references.

[2] After this work had been completed and prepared for publication, it was found that an important paper dealing with this subject, by J. Koenigsberger and O. Reichenheim (Centralbl. f. Min., 1905, p. 454) had been overlooked. These authors investigated the absorbing powers and electrical conductivities of molybdenite, stibnite, pyrite, galena, and iron sulphide; their work on conductivity furnishes the only data available for these materials, and will be quoted later in the discussion of the present results. On absorption, however, since they did not use spectral dispersion, but only employed screens to obtain comparatively large ranges of radiation—the total radiation in a given region of the spectrum being measured—their results are only approximate. These will be compared with those obtained by the writer for the various materials. Koenigsberger and Reichenheim state that they were usually only able to use small pieces (4×4 mm. in area) of the minerals: in the present work much larger pieces of stibnite and molybdenite were used, and they were also of quite uniform thickness; it must be stated, however, that Koenigsberger and Reichenheim have results for pyrite, which the present author found quite difficult to handle, so that no results are offered here for this material.

The bridge would ordinarily be balanced for zero radiation by shunting one of the arms, say R', with a more or less constant resistance R_1, and then, the bolometer strip B being exposed to the radiation, the deflection of the galvanometer deflection taken as directly proportional to the energy received by the strip. The present method, however, consists in balancing the bridge again by adjusting the shunt, and converting readings obtained in this way into relative changes of resistance in B, due to the incident radiation. If we determine the relative changes in the resistance of the strip produced by different quantities of energy falling on it, we have accurately the ratio between the two quantities of energy, if we make the single assumption (fundamental for all bolometric work) that the change in the resistance of the strip is directly proportional to the quantity of energy falling on it. If B were equal to B' and R to R' within very narrow limits, then a resistance of several thousand ohms as R_1 would suffice to balance the bridge; furthermore, a change of 0.1 ohm in R_1 would probably be the smallest convenient amount which would be detected by a good galvanometer, say of 10 ohms resistance and a sensitiveness of 10^{-9} ampere per scale division at a meter distance. In the present case however the strips B and B' were hurriedly made, and only adjusted to within about 1.5 per cent. of each other, so that it became necessary to use R_1 for balancing the bridge for zero radiation, and to add the supplementary resistance R_2 for the purpose of making the adjustments used in measuring the radiation.

For the sake of completeness we give here the numerical calculations relating to a definite set of values for the various resistances used. Several combinations were tried, but the one which seemed best adapted to the sensitiveness of the galvanometer was the following:

$B = B' \pm 1.5$ per cent. = ca. 4 ohms,
$R = R' = 20$ ohms,
$R_1 = 588$ ohms,
$R_2 = 4{,}800$ ohms (variable by increments of 0.1).

Given different changes in R_2 corresponding to different values of the resistance of the arm of the bridge (or different quantities of energy falling on B) we desire the relation between them. If the total resistance of the arm is denoted by R, then

$$\frac{1}{R} = \frac{1}{R'} + \frac{1}{R_1} + \frac{1}{R_2} = \frac{R_1 + R'}{R_1 R'} + \frac{1}{R_2} = a + \frac{1}{R_2}, \tag{1}$$

where $a = (R_1 + R')/(R_1 R')$ is kept constant. Differentiating,

$$dR = \frac{dR_2}{(R_2 a + 1)^2}, \tag{2}$$

which shows at once that dR_2 is quite different for equal changes dR if we consider two changes dR which are the first and last increments in a total change of, say, 100dR. We must therefore derive a convenient formula for correcting the observed readings dR_2: one would naturally expect that an additive per cent. correction would be easiest to apply to dR_2. Since dR_2 is now no longer an infinitesimal, but a considerable fraction of R_2 we must derive the formula rigorously from the beginning. Writing down (1) and increasing R and R_2 by dR and dR_2 respectively, we have

$$R = \frac{R_2}{1 + R_2 a}, \tag{3}$$

$$R + dR = \frac{R_2 + dR_2}{1 + (R_2 + dR_2)a}, \tag{4}$$

whence

$$dR = \frac{R_2 + dR_2}{1 + (R_2 + dR_2)a} - \frac{R_2}{1 + R_2 a}, \tag{5}$$

$$= \frac{dR_2}{(R_2 a + 1)^2 + a dR_2(1 + aR_2)}, \tag{6}$$

for which we may write

$$dR = \frac{dR_2}{(R_2 a + 1)^2}(1 - x), \tag{7}$$

in which x denotes the required per cent. correction. Equating the right-hand members of (6) and (7), we find that

$$x = \frac{a dR_2}{(1 + aR_2) + a dR_2}. \tag{8}$$

As $|a dR_2| < |1 + aR_2|$ we note that if dR_2 is negative, x is negative and therefore the correction is additive. To apply the correction, we first calculate

$$a = \frac{R_1 + R'}{R_1 R'} = \frac{1}{R'}\left(1 + \frac{R'}{R_1}\right).$$

Since a is approximately $1/R'$, or $1/20$, x is very nearly independent of a, and this approximate value of a is quite good enough to use in computing x. If we compute x as a function of dR_2 we have the following values which are plotted in Fig. 2.

$\frac{1}{a} = R' = 20$ ohms. $R_1 = 588$ ohms. $R_2 = 4{,}800$ ohms.

dR_2	$-x = \frac{-dR_2}{R' + R_2 + dR_2}$
− 100 ohms	+0.021
− 400	0.091
− 800	0.199
−1200	0.331

We can easily read from the curve the proper correction to apply to a given reading; *e. g.*, if dR_2 is 1,200 ohms we add 33 per cent. or multiply by 1.33 to obtain a number directly proportional to the change in resistance of an arm of the bridge. Assuming that the change in resistance is directly proportional to the energy falling on the strip, we then have a number directly proportional to this quantity of energy. Note in passing that, in case R_2 shunted an adjacent arm of the bridge and had to be increased, the correction would be a negative one, and relatively decreasing with increasing dR_2, *i. e.*, concave to the right instead of to the left.

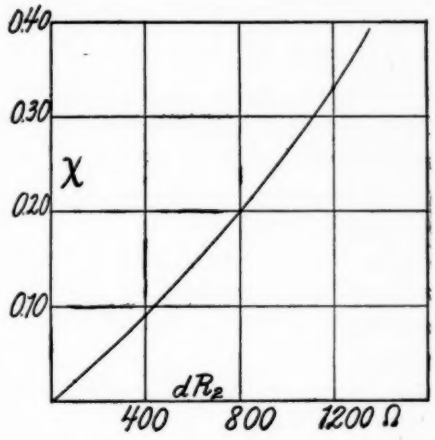

Fig. 2.

The following points in favor of this method of using the bolometer may be noted:

It does not assume that the current through the galvanometer is directly proportional to the change in the resistance of one of the bridge arms.

It is independent of changes in the sensitiveness of the galvanometer, and also of the position of the galvanometer zero, if this varies.

In passing through parts of the spectrum rich in energy, there is no abrupt change in the sensitiveness of the apparatus to radiation, as there would be if successive shunts or series resistances had to be thrown into the galvanometer circuit. In fact the double uncertainty of non-linear galvanometer scale and inaccurate shunts was what led the writer to try this balanced method. The non-linear scale, in particular, is a great disadvantage, which can scarcely be avoided as long as we have to use for measuring radiation galvanometers with small suspended system turning through relatively large angles. For these reasons this method should be peculiarly adaptable to running energy-spectrum curves.

Under favorable conditions as to steadiness of bolometer (using a very tightly enclosed vacuum-bolometer) one could easily read the energy at the maximum of an energy curve to one ten-thousandth part of itself. This condition was realized by the present writer, in the following measurements, as far as quantity of energy and sensitiveness was concerned, but not with regard to steadiness, as the bolometer was air enclosed, and,

in passing through the spectrum, the zero (that is, the value of R_2 necessary to balance for no radiation falling on the strip) was not determined after each reading, but only at intervals over the whole range. It takes time and patience to balance the bridge, but when accurate results are desired, it seems that this method may be valuable, although where the energy curve is flat and the quantity of energy relatively small (say for $\lambda > 10\mu$) it must be said that the deflection method yields about as accurate, and rather more easily obtained results.

ARRANGEMENT AND ADJUSTMENT OF THE OPTICAL APPARATUS.

The infra-red dispersion apparatus consisted of a rock-salt prism of angle 60° 1′ 8″ and faces 11 cm. by 7.5 cm. high, fitted with a Wadsworth mirror, the whole rotating with the 17-inch divided circle of a large spectrometer of the ordinary type. Two concave mirrors of 66 cm. focal length and 7.5 cm. aperture served as collimators, being rigidly mounted on arms of the spectrometer. The bolometer case was held by an independent massive support, as were also the slit and an external mirror (of 7.5 cm. aperture and 33 cm. focus) which was used to bring a real image of the source of light on the slit. When not in use a glass cover jar was fitted over the prism, and sealed with oil in an annular trough around the edge; a drying agent placed within assured a dry atmosphere surrounding the prism. This arrangement has been very satisfactory for a period of time of several months. The whole apparatus, then, does not differ from the ordinary infra-red prism spectrograph except perhaps in point of size.

The width of the bolometer strip has been given as 0.05 cm.; in most of the following work the slit was of the same width, and its length was such that the spectrum covered nearly all of the bolometer strip. In a few cases, however, the proportions of the slit were changed in order to try the transmission of a small specimen. A slit of width 0.05 cm. subtends an angle of 0.00076 radians or 2.7 minutes of arc, if viewed from the telescope mirror. This is equal to an extent in the spectrum of from 0.1μ to 0.5μ, depending on the dispersion. On the average, between 1μ and 7μ the strip may be considered as receiving the energy of a spectral region 0.25μ in extent.

For calibration, the D line was taken as a datum, and a curve was plotted showing the deviation from the position of the D line as a function of λ. The prism angle was carefully measured, and for the dispersion of the rock-salt, Paschen's[1] values were used. From the deviation curve, a scale of wave-lengths and angular rotation from the D line was con-

[1] Ann. d. Physik, 26, 1908, p. 128.

structed by projection on the drawing board. This scale was about 12 inches long for the region from $\lambda = 0.5896\mu$ to $\lambda = 7\mu$. For making the measurements rapidly, advantage was taken of a train of gears which connected the rotating prism-circle with a plate lowering apparatus, which was originally designed so that infra-red bolograms could be made by recording the galvanometer deflections on a moving sensitive plate. The graphically constructed scale was of such a length that when fitted to the plate-carrier (the whole apparatus being adjusted to the D line), the scale slid by a fiducial mark giving correct wave-length readings as the spectrum was made to march across the bolometer strip. A test of the scale usually gave the wave-length of the CO_2 absorption band within 0.02 or 0.03μ of its correct value ($\lambda = 4.38\mu$). Of course settings made with this scale cannot compare for accuracy with those made by means of a calibration curve and a reading microscope, but this would have been very tedious work for these measurements. The various gears between the plate carrier and the rotating circle introduced small errors of lost motion and uneven running which could not be eliminated. Taking into consideration all errors, it is estimated that the absolute position in the spectrum at any setting was known, on the average, to within 0.05μ, and any setting could be repeated (by turning back, and coming forward again until the same division was under the mark) to about 0.01μ. Some badly determined points may be noticed among the observations: the steep slopes of the energy curve near the atmospheric absorption bands at 2.1μ, 2.7μ, and 4.4μ were especially troublesome, and inaccuracies due to this cause cannot be avoided unless a setting can be repeated to within a few thousandths of a μ, which was impossible with the method and apparatus used by the writer.

As a source of light, a one-ampere A.C. Nernst filament operated somewhat below full capacity on a storage battery, was found to give the most constant radiation. After being used for some time, the A.C. glower (with leads fused in at each end) seemed to develop a very constant resistance. It may be stated that enclosing the source of radiation in a water jacket proved very effective for disposing of all the energy not thrown into the spectrometer by way of the collimating system.

No limiting diaphragm was used anywhere in the path of the beam. Practically, the prism face acted as such a diaphragm, as the beam from the collimator was so much larger than the prism face that the prism refracted only about 50 or 60 per cent. of the light, that is, the central portion. Since the light from the edges of the mirrors was thus lost, small errors in collimation, introduced by interposing specimens, had practically no effect on the position and intensity of the spectrum.

THE OBSERVATIONS.

In determining the per cent. of light transmitted through, or reflected by a given specimen, settings were made at intervals of about 0.1μ throughout the spectrum, and readings taken with the bridge balanced at each setting—thus obtaining measures of the relative quantities of energy at different wave-lengths. Then the spectrometer was turned back, the specimen interposed, the same settings repeated and the energy determined as before. The ratio was easily computed after the corrections earlier described were applied to the bridge readings.

If natural specimens are used it is hardly practicable to place them in parallel light; they must be placed where the beam is small, *i. e.*, near the slit. All the transmission specimens used by the present writer were placed perpendicular to the beam, and *behind* the slit. It is especially important for specimens of highly refracting material that they be placed, behind rather than in front of the slit, in order that the focus of the image of the energy-source on the slit shall be exactly the same with and without the specimen in place. For reflection the arrangement shown in Fig. 3

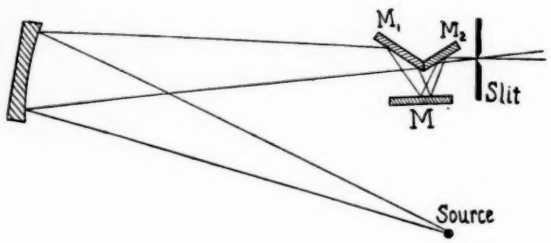

Fig. 3.

was used: the silvered mirrors M_1 and M_2 were fixed, and the mirror M, also silvered, could be removed and a surface of the material to be investigated substituted. The angle of incidence was here about 18°, which was practically normal incidence for materials of high refractive index. The reflecting power of the specimen was easily determined, using Hagen and Rubens'[1] values for the reflecting power of silver to correct the energy observed when mirror M is in place.

THE OPTICAL PROPERTIES OF SOME SULPHIDES.

Stibnite.—The observations on stibnite are given in Fig. 4. Two determinations were made of the reflection, and of the transmission of two different thicknesses. The curves are simply a mean, intended to

[1] Ann. d. Physik, 11, 1903.

be as consistent as possible with both sets of observations. This practice was followed with all the observations.[1]

Specimens of Japanese stibnite were used with natural, fresh cleavage surfaces. Stibnite crystallizes in the orthorhombic system, and is biaxial if like all known transparent crystals of this class. The cleavage

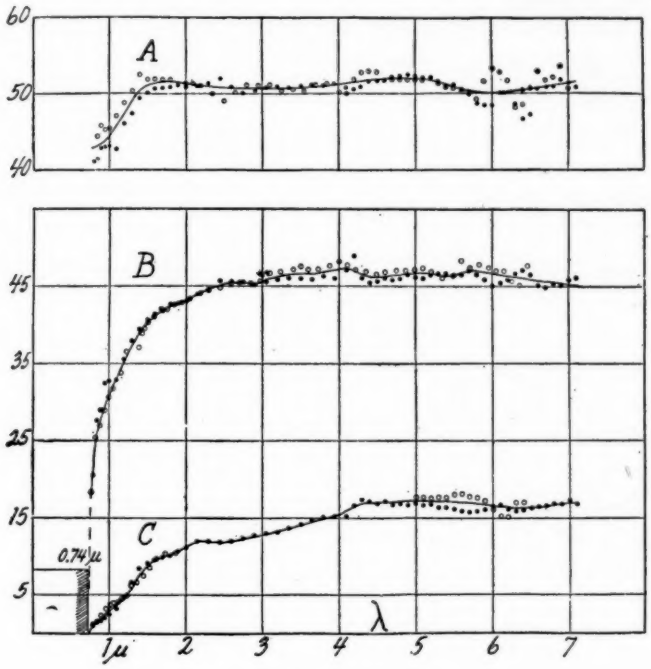

Fig. 4.

Curve *A*: Per cent. of energy reflected from stibnite.
Curve *B*: Per cent. transmitted through layer 0.18 cm. thick.
Curve *C*: Per cent. transmitted through layer 0.73 cm. thick.

is perpendicular to the crystallographic *b*-axis, so that the path of the light lay along this axis. The bisectrix of the optical axes of crystals of this type may lie along any one of the *a*, *b*, *c*, crystallographic axes, so that the optical constants here determined are for neither pure ordinary or extraordinary rays. They are offered merely as empirical relations which will have to serve for cleavage layers until this substance is more thoroughly investigated.[2] In Fig. 8 are given the values of the extinction-

[1] Koenigsberger and Reichenheim obtain somewhat lower values for transmission and reflection of stibnite. Coblentz, however (quoted in Wood's Optics, 2d ed., p. 400), obtains a value for transmission very close to that offered here.

[2] The following experiments by Prof. A. Trowbridge on the double refraction of stibnite may be of interest here:

A collimator system containing a glass lens, a slit, and a concave mirror was set up between

modulus[1] $n\chi$ computed from the observations on the transmission of the two thicknesses by means of the formula

$$n\chi = \lambda\alpha = \frac{\lambda \log J_1/J_2}{4\pi(d_1 - d_2) \log e}$$

in which α = the extinction coefficient,

J_2 = relative transmission of the thin piece,

J_1 = relative transmission of the thick piece,

d_1 = thickness of thick piece, and

d_2 = thickness of thin piece, measured with the micrometer caliper.

In the derivation of this formula the reflection from the first surface and one reflection from the last surface are eliminated. If a specimen acts as a Fabry and Perot interferometer, and by successive internal reflections contributes to the transmitted energy, we can only observe that on account of the thickness the resulting interference bands in the spectrum are so narrow that the bolometer does not resolve them, and only the mean energy is observed. This should be equal to the energy in the first transmitted ray, so that we are justified in placing confidence in the above given formula; furthermore the successive rays due to multiple internal reflections are rapidly extinguished by the increased absorption due to lengthening path in the material.[2]

The limit of transmission of a piece a fraction of a millimeter thick is at 0.74μ.[3]

a Nernst filament and a bolometer. In this collimator system were placed an analyzer and a polarizer consisting of transmission plates of mica, with their directions of greatest transmission crossed. Between analyzer and polarizer was placed a layer of stibnite which was rotated. There was no dispersion, total radiation through the glass lens being measured by the bolometer. On the stibnite cleavage surfaces there are striæ parallel to the crystallographic *a*-axis: it was found that when the layer was turned so that the striæ made an angle of 45° with the plane of polarization of the polarizer, about four times as much energy was transmitted as when the striæ were either perpendicular or parallel to the plane of polarization. This shows either that it is more transparent to a vibration making an angle of 45° with the striæ, or that in that case it gives rise to a circular vibration: either explanation would imply double refraction.

Again, the polarizer was removed, and a prism placed in the collimator system, thus converting it into a dispersion apparatus. The layer of stibnite was put in with its striæ parallel to the slit, and energy spectra observed with the analyzer set at different azimuths. It was found for wave-lengths less than 3μ (for which the glass lens was transparent) that more energy got through when the plane of vibration of the analyzer was parallel to the striæ than when perpendicular. This shows that its extinction coefficient is different for vibrations in different directions, or, that it acts like tourmaline to some degree, and may be used as an analyzer.

[1] We follow the notation of Kayser, Handbuch, III., p. 15.

[2] Koenigsberger and Reichenheim (loc. cit.) derive a more rigorous formula, taking into account the second reflections, but we do not carry the formula this far, for the reasons stated.

[3] A piece of stibnite transparent down to 0.7500μ at ordinary temperature became transparent to 0.7200μ on being cooled by immersing in liquid air.

No attempt to obtain the refractive index was made except in a very general way from the reflection observations. After 4μ the reflection and absoprtion curves are practically constant: since the value of $n\chi$ is so very low, we may obtain an approximate value for the refractive index by ignoring $n\chi$ and using the formula for reflecting power

$$R = \left(\frac{n-1}{n+1}\right)^2, \tag{9}$$

which, solved for n, gives

$$n = \frac{1}{1-R}(1 + R \pm \sqrt{4R}). \tag{10}$$

Using the larger root for n we calculate the following values:

λ	n
1.5μ	6.00
3.0	5.95
5.0	6.16
7.0	5.97

which are given simply as being in the neighborhood of those given by E. C. Müller, namely $n_{red} = 4.69$ and $n_{blue} = 5.53$.[1] The outstanding feature is of course the very small dispersion, and the constancy of the extinction coefficient α from about 2μ on, in the infra-red.

On the electromagnetic theory for absorbing bodies the relations[2]

$$n^2(1-\chi^2) = \epsilon, \tag{11}$$

$$N^2\chi = \sigma T, \tag{12}$$

should hold, in which ϵ is the dielectric constant, σ the conductivity in absolute electrostatic units, and T the time of one vibration. The writer is unable to find any data for the two electrical constants, but the following table, calculated from the values of n and $n\chi$ may be of some use (we take $n = 6.00$ for these values of λ):

λ	n	$n\chi$	$\sigma = n^2\chi/T$
1.5μ	6.0	3.35×10^{-5}	4.0×10^{10}
3.0	6.0	$5.6\ \ 10^{-5}$	$3.3\ \ 10^{10}$
5.0	6.0	$7.2\ \ 10^{-5}$	$2.6\ \ 10^{10}$
7.0	6.0	$10.0\ \ 10^{-5}$	$2.6\ \ 10^{10}$

A conductivity of 3×10^{10} electrostatic units is equal to a resistance of 30 ohms per cubic centimeter.

[1] Wood, Physical Optics, 2d ed., p. 400.

[2] Drude, Lehrbuch d. Optik, 2d ed., p. 341.

Sphalerite.—The observations on this substance, the natural sulphide of zinc, are given in Fig. 5. Sphalerite is isometric (optically isotropic) and all cleavages should give specimens with the same optical properties. The material is marred by a yellow coloring and resinous streaks due to

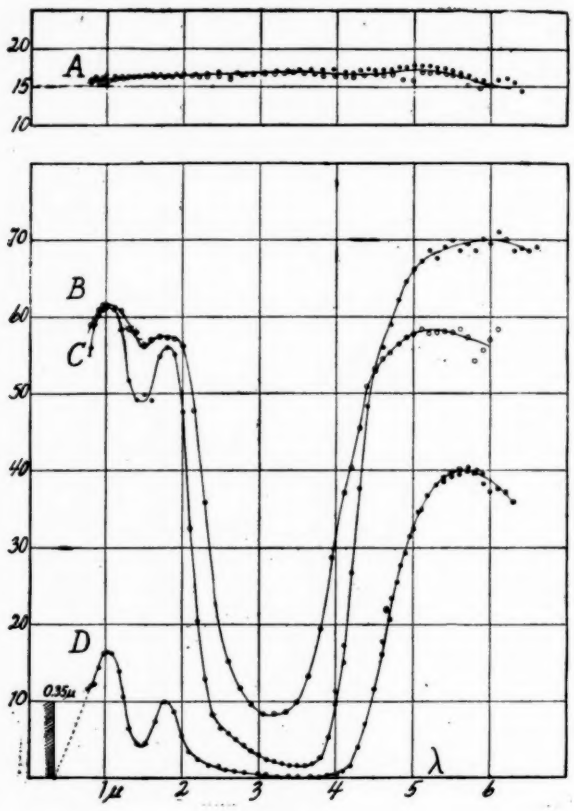

Fig. 5.

Curve *A*: Per cent. of energy reflected from sphalerite.
Curve *B*: Per cent. transmitted through layer 0.067 cm. thick.
Curve *C*: Per cent. transmitted through layer 0.253 cm. thick.
Curve *D*: Per cent. transmitted through layer 1.68 cm. thick.

the presence of iron and manganese sulphides, which crystallize isomorphous with the sphalerite. With regard to the curves, the crossing of *B* and *C* at $\lambda = 4.5\mu$ may be explained by the fact that *B* is from a very small specimen, which necessitated using a short and wide spectrometer slit in running the curve. *B* is offered simply for its interest near the absorption band at 3.2μ. The fact that *D* is so much lower than *C* for $\lambda < 3\mu$ is probably due to a much greater quantity of the brown impurity in the thick specimen. The values of $n\chi$ computed from curves *C* and *D*

are given in Fig. 8. The limit of transparency of a piece about 0.5 mm. thick was determined by the writer with the aid of an ultra-violet spectrograph and found to be about at 0.35μ. It is practically impossible to determine the refractive index of sphalerite in the infra-red without polishing acute prisms of the material. Experiments made by the writer show that a polish even approaching the perfection of a cleavage surface is out of the question, as the material is comparatively soft; its hardness on the Moh scale being about 3.7. The refractive index is so high ($n_{green} = 2.4007$, $n_{yellow} = 2.3692$, $n_{red} = 2.3417$[1]) that natural cleavage prisms (of angle 60°) are of no use, even if they could be obtained of sufficient size.[2]

The absorption bands determined at 1.5μ and 3.2μ should be characteristic of pure sphalerite. According to numerous analyses, no water of crystallization or of combination is contained in the material.

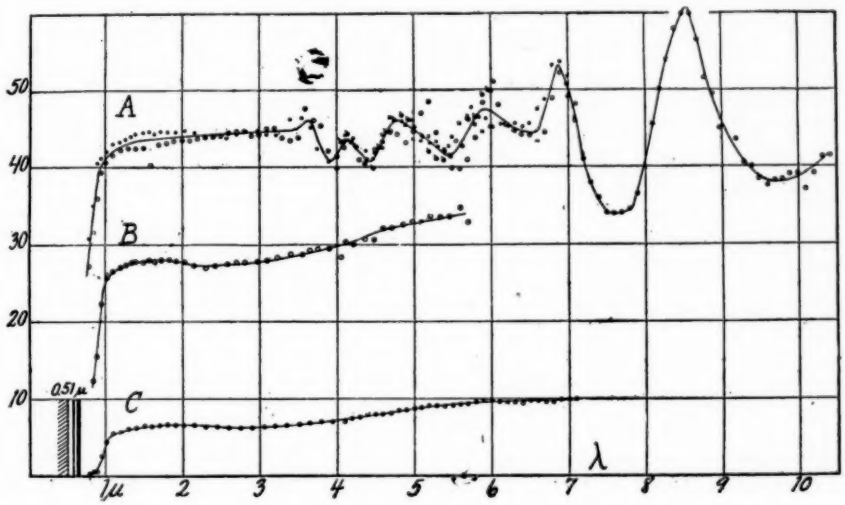

Fig. 6.

Molybdenite.

Curve *A*: Per cent. transmission of a layer 4.2μ thick.
Curve *B*: Per cent. transmission of a layer 0.0246 cm. thick.
Curve *C*: Per cent. transmission of a layer 0.0769 cm. thick.

Molybdenite.—This is the most interesting of all the sulphides in its optical properties. Its crystals are hexagonal, with basal cleavage allowing specimens of almost any thinness to be obtained. Hexagonal

[1] Ramsay, Zt. f. Kryst., 12, 1887, p. 218.

[2] We have no data that will enable us to test the relation $n^2\chi = \sigma T$. Doelter (Sitz. Ber. d. Kais. Akad., Wien, 119, I., 1910, p. 49) states that "zinc sulphide, even when heated to 420° (when it decomposed) showed practically no conductivity."

crystals are doubly refracting, uniaxial with the optic axis along the crystallographic c-axis, that is, perpendicular to the cleavage planes. Therefore in determining the optical constants for light passing along the optic axis, we have to deal only with the ordinary ray, and any constants that we can determine in this way are the true ones for the ordinary ray. The observations for the relative transmission are given in Fig. 6. The wavy character of Curve A is very striking and at once suggests interference. That this is interference is proved by the fact that the spacing of the bands varies with the thickness of the specimen. In Fig. 7 Curve A gives the energy reflected from a piece slightly thicker;[1] the bands are closer together, as they should be.

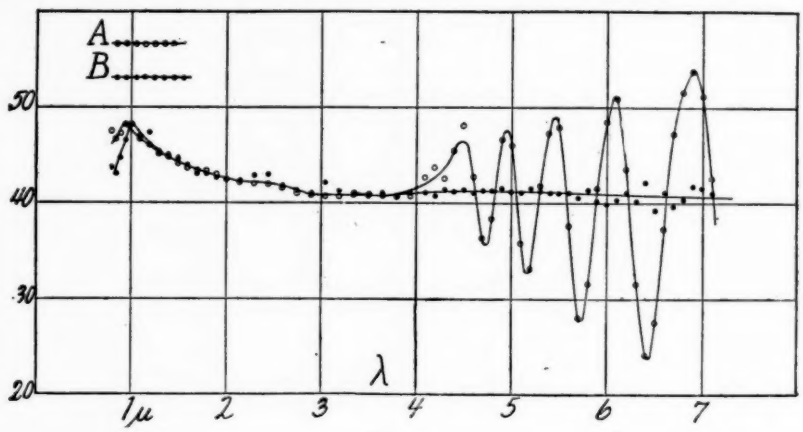

Fig. 7.

Molybdenite.

Curve A: Per cent. of energy reflected from a layer 6.6μ thick.
Curve B: Per cent. of energy reflected from a layer 34μ thick.

Both of these also showed interference in the visible region as will be discussed later. A very thin specimen (about 1μ thick) gave the absorption spectrum shown in the lower left-hand corner of Fig. 6, the limit of transmission being at about 0.51μ. Besides the 3 curves shown in Fig. 6 a fourth might have been given showing the transmission of a piece 34μ thick, but this is omitted, as it is practically identical with Curve A except in the matter of interference. The light reflected from this piece is given in Curve B, Fig. 7, which is also identical with A, Fig. 7, except for the interference. The values of $n\chi$ given in Fig. 8 are computed by the usual method from Curve A (using mean values where it oscillates) and Curve C, Fig. 6.

[1] Koenigsberger and Reichenheim (op. cit.) give a reflecting power for molybdenite much lower than this.

The determination of the thickness of the very thin pieces of molybdenite is somewhat difficult by ordinary methods. Any method involving pressure is apt to damage the specimen, so that recourse was had to the method of weighing, the specific gravity having been determined and the area of the piece being computed.

To produce a good cleavage surface for reflection, it was necessary to split a thin layer of the material and squegee it down onto a piece of plate glass by rubbing it lightly with a pad of cotton, thus securing a fairly plane surface and good definition.

We proceed to consider the interference phenomena exhibited by the thin layers of this material. When a thin film is placed in front of the slit of a spectrometer, the positions and the spacing of the resulting interference bands in the spectrum afford a means of finding the dispersion of the material of the film. For a dark band at λ_1 the following relations must hold:

$$2n_1t = (N_1 + \tfrac{1}{2})\lambda_1;$$

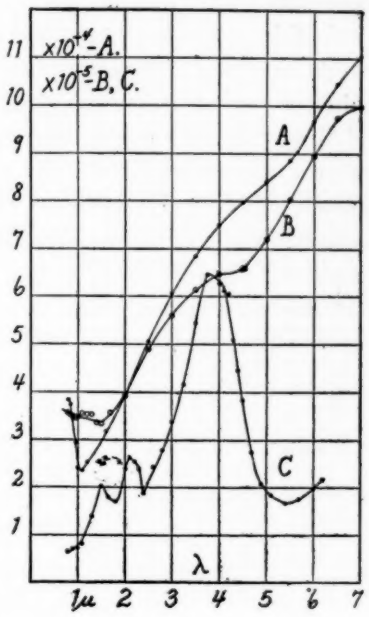

Fig. 8.
Curve A: $n\chi$ for molybdenite.
Curve B: $n\chi$ for stibnite.
Curve C: $n\chi$ for sphalerite.

similarly for a dark band at λ_2

$$2n_2t = (N_2 + \tfrac{1}{2})\lambda_2, \qquad (14)$$

in which n is the refractive index, N a certain integer, and t the thickness of the film. For neighboring bands, that is, for two values of λ close together, we assume that dispersion is not an important factor, and consider that the bands occur simply on account of the varying relation between λ and $2nt$; we may then take $n_1 = n_2 = n$ and easily derive the following formula from (13) and (14) by subtraction:

$$N = 2nt\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right), \qquad (15)$$

in which $N = N_1 - N_2$, the change in N_1 in passing from λ_1 to λ_2, and is equal to the number of bands between λ_1 and λ_2. This may be written

$$n = \frac{N\lambda_1\lambda_2}{2t(\lambda_2 - \lambda_1)}. \qquad (16)$$

The formula is only approximate on account of the real variation of n with λ, but it will be seen that if n varies slowly it should hold over short ranges; moreover, if n should vary rapidly and *increase* as λ *decreases* the bands will naturally come close together, so that we might even use it in this case, if we take only one or two bands as an interval.

We give the following data on the position of interference minima for films of various thicknesses. The infra-red observations are from Curve *A*, Fig. 7, and Curve *A*, Fig. 6. The observations in the visible region were made with the aid of a Hilger wave-length spectrometer and are means of several settings. The bands should of course be regularly spaced from the visible on into the infra-red region; since however the width of the bolometer strip was such that in the region from $2-3\mu$ it covered an extent of about 0.5μ in the spectrum, the bands are so closely spaced that they cannot be resolved.

	Transmission.		Reflection.
Thickness.....	(1) 4.2 μ.	(2) 2.2 μ.	(3) 6.6 μ.
Positions of interference minima....	0.7141 μ	0.7001 μ	
	0.7208	0.7101	
	0.7286	0.7228	
	0.7361	0.7379	
	0.7453	0.7557	
	0.7555	0.7751	
	0.7658		
	0.7759		
	3.45		4.75
	3.95		5.18
	4.45		5.75
	5.40		6.45
	6.45		7.38
	7.65		
	9.80		

Applying the formula successively to the visible readings in set (1) taking two fringes as the interval, and to set (2), taking 1 fringe at a time, and taking for λ the mean of λ_1 and λ_2, we compute the following:

λ	n Set (1).	n Set (2).	λ	n Set (1).	n Set (2).
0.7050		11.3	0.7453	6.84	
0.7164		9.17	0.7468		7.12
0.7208	8.54		0.7555	6.63	
0.7286	8.25		0.7654		6.87
0.7304		8.02	0.7658	6.85	
0.7361	7.74				

Assuming that n is practically constant between $\lambda = 3.5\mu$ and 10μ, as reflection and transmission curves are horizontal here, and calculating a mean value of n, using the first and last only of the infra-red observations, we have

From set (1), $n = 4.2$
From set (3), $n = 4.04$
Mean 4.1

In order to utilize the single readings we observe that the difference in optical length of path which gives rise to the interference is for the transmission piece (1) $2nt$ or about 34.4μ and for the reflection piece 54.3μ. For transmission the path difference should be equal to an odd number of half wave-lengths, and for reflection, an even number (taking into account the phase change of $\lambda/2$ of the directly reflected ray) in order to produce a minimum. By trial the following numbers are found to satisfy this condition approximately, and on assuming that they do exactly, the retardation $2nt$ can be calculated for a given value of λ and hence a value of n_λ found, $2t$ being known.

Set (1) Transmission.				Set (3) Reflection.			
λ	Number, N.	$N\lambda = 2nt$.	$\therefore n$.	λ	Number, N.	$N\lambda = 2nt$.	$\therefore n$.
3.45	9.5	32.8	3.9	4.75	11	52.3	3.98
3.95	8.5	33.5	4.0	5.18	10	51.8	3.95
4.45	7.5	33.4	4.0	5.75	9	51.8	3.95
5.40	6.5	35.1	4.2	6.45	8	51.6	3.93
6.45	5.5	35.4	4.2	7.38	7	51.6	3.93
7.65	4.5	34.4	4.1				
9.80	3.5	34.3	4.1				

We now have approximate values for n over a short range of the visible and a considerable region of the infra-red. The dispersion is given in Fig. 9, Curve A; a larger scale is used for the values in the visible region. In drawing the curve more weight is given to the values from set (3) on account of the very accurate spacing of the interference bands in the reflection-specimen. The transmission specimen is undoubtedly of slightly varying thickness, which accounts for the relatively poor determination of the interference bands observed. By weighing, of course, only a mean thickness is determined. With regard to the accuracy of the method, it should give good results under favorable conditions: that is, with a perfect Fabry and Perot interferometer in front of the infinitely narrow slit of a perfect spectrometer. At any rate, allowing for the unevenness of films, wide slits, etc., which are unavoidable with these

specimens, the values of n should be correct within 5 or 10 per cent. From the reflection curve, taking the limiting value of 41 per cent. reflected light, and using formula (10), we compute $n = 4.5$ which is not far from the value obtained by means of the interference observations.

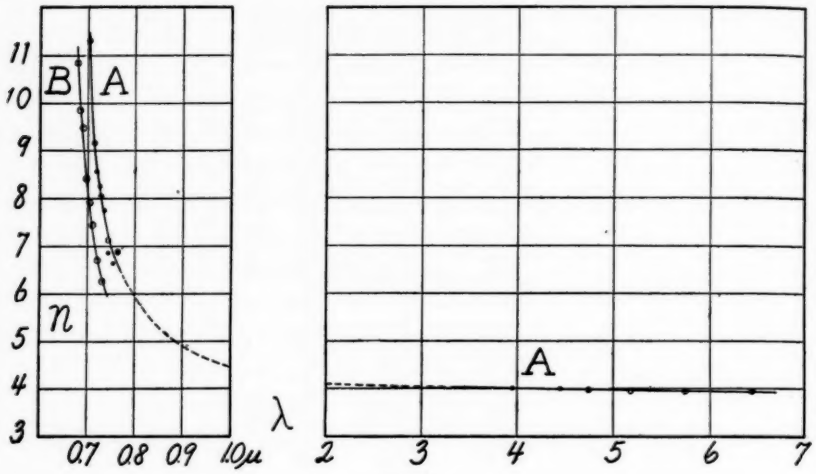

Fig. 9.

Curve *A*: Dispersion of molybdenite at ordinary temperature.
Curve *B*: Dispersion at temperature of liquid air.

The relation $n^2\chi = \sigma T$ may be tested for this substance. Calculating $\sigma = n^2\chi/T$ for several values of λ for which we have n, we find:

λ	n	$n\chi$	$\sigma = n^2\chi/T$
0.80 μ	6.00	3.9×10^{-4}	8.60×10^{11}
3.0	4.02	$6.1\ 10^{-4}$	$2.45\ 10^{11}$
4.0	4.0	$7.5\ 10^{-4}$	$2.25\ 10^{11}$
5.0	3.98	$8.4\ 10^{-4}$	$2.00\ 10^{11}$
6.0	3.94	$9.7\ 10^{-4}$	$1.91\ 10^{11}$
7.0	3.90	$11.0\ 10^{-4}$	$1.85\ 10^{11}$

A conductivity of 2×10^{11} electrostatic units is equal to a resistance of 4.5 ohms per c.c. Prof. A. Trowbridge, of Princeton, and Prof. G. W. Pierce, of Harvard, have made determinations of the specific resistance of this material which are, respectively, 3 ohms and 6 ohms per c.c.[1] at ordinary temperature (ca. 17° C.).

Through the courtesy of Professor Trowbridge the writer is enabled to

[1] Koenigsberger and Reichenheim (op. cit.) give for the resistance of molybdenite 3.06 ohms at 17° C. in the direction of the *C*-axis (the direction of light propagation in the present work). They also find that the conductivity increases rapidly with rising temperature. Pierce's data for the resistance of a molybdenite rectifier (PHYS. REV., 28, 1909, p. 151) exhibit this effect in a very striking manner.

communicate the following details regarding the optical properties of molybdenite at low temperatures:

A piece 4 or 5μ thick which was transparent down to 0.7020μ became transparent to 0.6660μ at the temperature of boiling liquid air (−190° C.).[1]

A piece 4.1μ in thickness was kept immersed in liquid air and the interference bands in the visible region found with the aid of a concave grating to lie at the wave-lengths

0.7430μ	0.7130	0.6911	0.6750]
0.7320	0.7053	0.6854	0.6720
0.7220	0.6977	0.6795	

The writer is unable to find data on the coefficient of expansion of molybdenite, but neglecting the effect of expansion on the thickness of the film, we compute, using formula 16, taking two bands at a time, the following values of the index:

λ	n
0.6757μ	14.8
0.6802	10.85
0.6853	9.86
0.6915	9.48
0.6982	8.40
0.7054	7.92
0.7136	7.44
0.7225	6.70
0.7325	6.24

This dispersion is plotted in Fig. 9, Curve *B*. The refractive index cannot possibly be independent of the temperature unless the coefficient of expansion is in the neighborhood of 0.001, which would be very high, say from 3 to 5 times as great as that of metals. The general facts set forth here agree very well with what Pulfrich found for glasses—namely, as the temperature fell, the ultra-violet absorption band moved toward the ultra-violet end of the spectrum, and the dispersion was decreased.

Other Sulphides.—Some other sulphides were ground into thin plates and tested qualitatively for transparency in the region $1\mu < \lambda < 6\mu$. It was difficult to produce thin layers of any accuracy and polish, but as the materials seemed to be opaque, no further attention was given them. The results are given in this table:

Material.	Thickness of Layer.		
Covellite, CuS,	about 0.2 mm.	Opaque, $\lambda < 6\mu$.	
Chalcocite, Cu_2S,	about 0.5 mm.		
Galenite, PbS,	about 0.5 mm.		
Bismuthinite, Bi_2S_3,	about 0.2 mm.	Opaque in visible.	Sample too small for infra-red work.

None of these specimens became transparent when cooled in liquid air.

[1] Koenigsberger and Reichenheim established the fact that the transmission of total radiation by this substance was at 110° only 62 per cent. of the value at 40°. With regard to the

Koenigsberger and Reichenheim offer data on the reflecting power and transmission of pyrite, iron sulphide, and marcassite. They could not obtain similar films of galenite.

CONCLUSION.

While we have given approximate values for the refractive indices of stibnite and molybdenite, it is greatly to be desired that more accurate measures be made of these constants in the infra-red region. It is possible that very acute prisms of these materials could be filed out, and used in connection with a small spectrometer of short focal length. A prism of 1 or 2 mm. base would probably let through enough energy (where the energy spectrum is rich) to permit measurements by the method of minimum deviation.

A good determination of the electrical constants—conductivity and dielectric constant—is also necessary if much is to be done with these minerals.[1]

In molybdenite and stibnite we have two substances which in the near infra-red region have properties very much like those of ordinary transparent bodies in the visible—with the additional features of high refractive index and continued transparency for an indefinite distance with increasing wave-length. A two-term dispersion formula was applied to the dispersion curve of molybdenite, with the result that no solution for an absorption band in the distant infra-red could be obtained. Perhaps a method will be found for measuring the refractive index of the extraordinary ray in molybdenite, and determining the three refractive indices of stibnite. These results would be of great interest from a theoretical point of view.

A film of molybdenite a few microns thick offers possibilities with light of wave-length about 20μ for an investigation of the optical behavior of the film when twice its thickness is optically less than one wave-length.

The writer is under obligation to Prof. Augustus Trowbridge for suggesting this work, and for help and criticism throughout its progress. Prof. A. H. Phillips, of Princeton, has very kindly placed at the disposal of the writer his knowledge of mineralogy and crystallography and furnished an unusual crystal of sphalerite for this work.

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relation between conductivity and optical properties, it is well known that many oxides, sulphides, and other minerals which are poor conductors at ordinary temperatures become much more conducting when heated. For quartz and some other oxides, Doelter (op. cit.) found enormous decreases in resistance for specimens heated to 1300° C.

[1] Koenigsberger and Reichenheim give the conductivity of molybdenite (and its variation with temperature) in both crystallographic directions. They also give the conductivities of some of the other sulphides, but not of stibnite.

THE FLOW OF AIR THROUGH CAPILLARY TUBES.

By I. M. Rapp.

§ 1. The Problem.

A LARGE amount of work has been done on the flow of gases through capillary tubes, but most of it, especially that of recent years, has been done, not to secure an absolute value of the coefficient of viscosity, but rather to learn the law of temperature variation, the relative viscosities of gases, or of mixtures of gases, or finally, to find the point of "breakdown" of Poiseuille's law when the gas is driven through the tubes under very high or under very low pressure. With few exceptions, those later writers who have made absolute determinations of the viscosity coefficient give either very little data, or else such a wide range of variation in the separate trials, that it would be impossible, in trying to determine a probable value for the coefficient, to give, to each observer, a value proportionate to the accuracy of his work.

The chief difficulties encountered and the most probable causes of this great variation are found (1) in the smallness of the capillaries used, (2) in the irregularities of the bore, (3) in the method of calibration of the tube, (4) in the use of too large a driving pressure and (5) in the experimental difficulties such as the measurement of the volume and pressures and the holding of the latter constant.

Table I. gives a resumé of the best absolute determinations of the coefficient of viscosity of air which have been made by the capillary tube method. Nearly all of these observers have used tubes varying in radius from .05 mm. to .16 mm., while only one used a tube of radius greater than .22 mm.

A small radius means a decrease in the accuracy of its determination and since it enters in the fourth power in Poiseuille's law the error in the final result is increased in proportion. The development of the law is based on the assumption that the flow is in a tube of constant radius. This is an ideal condition which is seldom even approximated in tubes of small radius. In general, the bore of a capillary tube is conical, with minor variations from one end to the other. The solution of the equation for flow in a tube of varying conical bore has been neither made nor applied experimentally.

It has apparently been assumed by all of the earlier writers and by

some of the later, that the R of Poiseuille's law can be determined from the length and mass of a column of mercury which will fill the tube. This assumption is erroneous. *It must always yield too high values of η, since it assumes that the resistance offered by the tube to the flow of fluid through it is inversely proportional to the cross-section instead of to the square of the cross-section.*

TABLE I.

Previous Absolute Determination of η, Reduced to 15° C.

	Author.	Reference.	Length of Capillary.	Radius of Capillary.	$\eta \times 10^7$
1	Grindley and Gibson	Proceedings of the Royal Society, Vol. 80, p. 114, 1908.	3298 cm.	.1585 cm.	1,783
2	Schultze	Annalen der Physik, Vol. 5, p. 140, 1901.	52.541	.0075717	1,811
3	Tanzler	Ber. d. D. Phy. Ges., Vol. 8, p. 222, 1906.	52.040 52.4074	.007564 .00694717	1,812
4	Fisher	Physical Review, Vol. 28, p. 73, 1909.	49.6	.00548	1,785
5	Rankine	Proceedings of the Royal Society, Vol. 83, p. 275, 1909.	49.06	.010230	1,799
6	Breitenbach	Annalen der Physik, Vol. 67, p. 803, 1899.	55.82 95.43	.010661 .01381	1,809 1,804
7	Piwnikiewicz	Physikalische Zeitschrift, April, 1913.	36.55	.01772	1,796
8	Von Obermayer	Sitz. Ber. d. K. Ak. d. Wiss., Vol. 73, p. 433, 1876.	39.4 50.2 36.0 39.7	.0138 .0196 .02241 .01525	1,751
9	Schneebli	Arc. des Sci. Phys. et Nat. Genève, Vol. 14, p. 197, 1885.	39.95 85.06 43.61	.01236 .01625 .01090	1,871
10	O. E. Meyer	Die Kinetische Theorie der Gase, p. 189.	50 to 150	.0161 .00595 to .00710	1,750 to 1,820
11	Warburg	Annalen der Physik, Vol. 159, p. 399, 1876.	74.9 28.5	.015076 .009056	1,840 1,850
12	Puluj	Sitz. Ber. d. K. Ak. d. Wiss., Vol. 69, p. 287, 1874.	155.76	.0197353	1,863

Of the results shown in Table I., that of Grindley and Gibson is open to the least criticism. The remaining observers may be divided into two classes. First, No. 2 to No. 5, inclusive, who have made allowance for the irregularities in the bore of the tube, and second, No. 6 to No. 12, who have calibrated their tubes from the mass of a column of mercury

which will fill it. The results of O. E. Meyer show no consistency, while those of Puluj and of Warburg are so out of line with the findings of all other experimenters as to be unquestionably in error by several per cent.; probably because of bends in the capillary and inequalities in the bore. The difference in the results of von Obermayer and of Schneebli is due to the one making allowance for the vapor pressure of the water used in securing the driving pressure while the other does not. If the data of both are treated the same way, identical values are given. The experimental work of Breitenbach and of Piwnikiewicz seems to have been done very carefully, but as they assume a uniform bore their results cannot be accepted as accurate absolute determinations. The variation in the result given by the observers in the first group is not due primarily, as is shown in § 3, to the theory in the methods of calibration, but rather to the experimental difficulties in calibrating tubes which are of the order of .0075 cm. radius and to the difficulties of maintaining the experimental conditions constant. In addition to this, the method which Rankine used to secure his driving pressure introduces errors which cannot be corrected.

The stream lines within the capillary are parallel to the wall when the driving pressure is small, but in the vessels at the ends of the tube they are radial. The development of Poiseuille's law does not take account of the energy in these radial lines. This suggests that there is a fall of pressure within the vessel at the ends of the tube. M. Brillouin and W. J. Fisher have independently developed expressions[1] for this correction which becomes appreciable in a tube 1 m. long and .13 mm. radius when the driving pressure is greater than 10 cm. of mercury. Fisher has applied his formula to his own data and finds the correction to be negligible. In Schultze's and Breitenbach's data the correction is .1 per cent. The data of Grindley and Gibson require no correction as they measured the pressures at points within the tube at such distances from the ends that the stream lines were parallel. The lengths and diameters of the tubes and the driving pressures used show that the correction should be made to the results of some of the other observers, but it is impossible to do so, as the data given are insufficient. Brillouin's correction has not been applied by any one.

The determinations of the coefficient of viscosity which have been made by other methods agree more closely with one another than with those secured by the use of the capillary tube. Further, the accuracy of the value of the elementary electric charge,[2] as determined by the method

[1] See § 5.

[2] Millikan, PHYS. REV., Vol. 32, p. 349, 1911.

developed by Professor R. A. Millikan, depends on the absolute value of the coefficient of viscosity. Since in that method η is the factor whose value is most in doubt, it became necessary that it should be redetermined with the greatest accuracy possible. Hence the following investigation was undertaken with a view of eliminating, as far as possible, the sources of error incidental to the capillary tube method and of seeing whether or not it is capable of yielding a value in agreement with that found by other methods. The distinct features of the research are:

1. The selection of very uniform tubes.

2. The use of a considerable number of tubes of quite different dimensions.

3. The accurate calibration of these tubes.

4. The use of small but constant and accurately measurable driving pressures.

5. The experimental study of the end correction.

§ 2. Selection of Tubes.

The tubes used, which were made of Jena glass, were selected for their circularity of cross-section and uniformity of bore so that the first two probable sources of error mentioned above might be made as small as possible. Those whose cross-section showed ellipticity when viewed under a twenty-power microscope were immediately cast aside and none were accepted unless the axes were shown by micrometer measurements to be approximately the same. The tubes which were broken in a later part of the research showed the same circular cross-section. The uniformity of bore was tested and only those tubes which showed neither sharp and abrupt changes nor large variations in their diameter were finally chosen. The tubes were cleaned by forcing through them solutions of potassium bichromate in sulphuric acid, potassium hydroxide, nitric acid and distilled water. During the process of cleaning they were kept at the temperature of steam by surrounding them with a jacket through which a current of steam was continually passing. One end of the tube was immersed in the cleansing liquid while the other extended into a flask which could be exhausted by means of an air pump. After the nitric acid had been washed out with the distilled water, absolute alcohol and dry air were driven through in order to remove the moisture. The bore was carefully examined for particles of dirt and the process of cleansing repeated until the tube was clear. As a further check it was recleaned after a number of viscosity determinations had been made. The fact that the same results were secured after recleaning was taken as proof that the tube was clean.

§ 3. Calibration of Tubes.

There are three methods by which the R of Poiseuille's law may be determined. The first is by the simple method of measuring the length and mass of a column of mercury which will fill the tube. The second was developed by Schultze[1] and consists experimentally in finding the value of L/R^4 from the volume and length of a short column of mercury at positions every two centimeters along the tube. The calibrating factor is computed from the equations:

$$\frac{L}{R^4} = \sum_0^L \frac{l}{r^4} = \frac{\pi^2}{v^2} \sum_0^L \lambda^2 l \tag{1}$$

and

$$v = \frac{U}{\sum_{l_1}^{l_2} \frac{l}{\lambda}}, \tag{2}$$

in which λ, r and v are respectively the length, radius and volume of the calibrating thread, l is the length of a portion of the tube over which the radius is assumed to be constant and U is the entire volume of the tube between the points l_1 and l_2. The third method was proposed by Fisher[2] and experimentally is identical with Schultze's. But his development is different, as he assumes that the radius is constant over an infinitesimal length, dl, of the tube and that the square of the fall in pressure over this length is dp^2. From these considerations he shows that

$$\frac{L}{R^4} = \frac{\pi^2}{U^2} \int_0 \lambda^2 dl \left[\int_{l_1}^{l_2} \frac{dl}{\lambda} \right]^2. \tag{3}$$

The values of the integrals are computed from the areas of the two curves formed by plotting λ^2 and $1/\lambda$ with l. Although developed by different methods, the two calibration equations are theoretically identical if we assume that the radius is constant over the same length of tube. In equations (1) and (2) l thus becomes dl and the summations become integrals. The combination of equations (1) and (2) is then identical with equation (3).

The tubes used in the absolute determination of the coefficient of viscosity were calibrated by Fisher's method. A check on the accuracy on his formula for the determination of the volume of the calibrating thread was had in the calibration of tube No. 4, by comparing the volume of the thread, obtained from its mass and density, with that computed by the formula

[1] Schultze, Annalen der Physik, Vol. 5, p. 140, 1901.

[2] Fisher, Phys. Rev., Vol. 28, p. 73, 1909.

$$v = \frac{U}{\int_{l_1}^{l_2} \frac{dl}{\lambda}}.$$

A difference of .2 per cent. between the two values was found. As this was less than the estimated error in the weight, Fisher's formula was considered to give the true value of v.

TABLE II.

The Radii of the Tubes Computed by the Different Methods of Calibration.

Tube No.	By Mass of Column of Hg.	By Schultze's Calibration.	By Fisher's Calibration.	Per Cent. Change in η by the Use of R of Column No. 2.
1	.023356 cm.		.023352 cm.	+0.01
2	.0129288		.0129214	+0.23
3	.0057800	.0057586 cm.	.0057581	+1.5
4*a*	.0251106	.025012	.025012	+1.7
4*e*	.0251106		.0251110	−0.01
5	.017119		.017114	+0.1
6	.0056551		.0056419	+1.0

In Table II. are given the values of the radii computed by the different methods. Only two tubes were calibrated by Schultze's formula. Both results were identical with those given by Fisher's method. If column No. 2 is compared with column No. 4, it is seen that the calibration by the use of the mass of the total column of mercury yields in every case too high a value of R and hence too high a value of η, as it should in view of the theoretical considerations mentioned above. The last column shows how much too high even with the use of these very uniform tubes the value of η would have been if this method of calibration had been used.

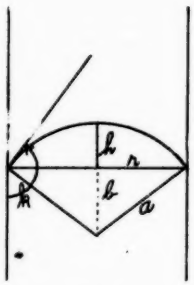

Fig. 1.

Both Schultze and Fisher in their methods of calibration consider that λ is obtained by adding one half the height of the meniscus to the apparent length of the mercury thread. This is true if the radius of the tube is small and consequently the height of the meniscus small, but will not be true if the tube is large.

The method of allowing for the meniscus in the larger tubes which were calibrated for this problem was as follows:

In Fig. 1, let r be the radius of the tube,

a be the radius of the spherical segment,

h be the height of the meniscus,

A be the area of cross-section of the tube,
V be the volume of the segment,
K be the angle of contact between glass and mercury,
$K = 141° 8'$.

From the figure

$$b = a - h = a \cos 51° 8',$$
$$r = a \sin 51° 8',$$
$$A = \pi r^2 = \pi a^2 \sin 51° 8',$$
$$a = h + b = h + a \cos 51° 8',$$
$$a = \frac{h}{1 - \cos 51° 8'},$$
$$V = \pi \left(\frac{2a^3}{3} - a^2 b + \frac{b^3}{3} \right).$$

The mean height of the meniscus, V/A, then becomes, when the substitutions are made, 0.53 h. A variation of several degrees in the angle of contact does not change the result more than one per cent., a variation which is negligible and which would allow for the assumption in the figure that the wall of the tube is parallel to its axis. The thread of mercury may be considered to be the frustum of a right circular cone capped by portions of spheres as described above.

If r is the radius at the middle point, Δr the difference between r and the radii of the ends, v the total volume of the thread and λ_1 the length of the thread between the menisci,

$$v = \pi \lambda_1 \left(r^2 + \frac{\overline{\Delta r^2}}{3} \right) + (V_1 + V_2).$$

Let λ be the length of a right circular cylinder of radius r and volume v.

$$v = \pi r^2 \lambda = A\lambda.$$

The solution of these two equations gives

$$\lambda = \lambda_1 \left(1 + \frac{\overline{\Delta r^2}}{3r^2} \right) + \left(\frac{V_1 + V_2}{A} \right).$$

$\overline{\Delta r^2}/3r^2$ is an exceedingly small fraction.

A difference of not less than 6 per cent. in the radii of the bases of the frustum is necessary to cause a change in λ which can be determined by the dividing engine. Since the actual variation in the tubes did not even approach this value, the thread of mercury can be considered as a cylinder and the radius of the tube, over this length, a constant. The expression $(V_1 + V_2)/A$ then becomes 0.53 $(h_1 + h_2)$ and

$$\lambda = \lambda_1 + .53\,(h_1 + h_2).$$

With the tubes of smaller radius, where h is small compared to λ no appreciable error is made in taking $\lambda = \lambda_1 + \frac{1}{2}(h_1 + h_2)$.

The theoretical value of V/A as determined above only approximates the true value of h. An exact mathematical expression cannot be obtained, as h is not the simple function of K which has been assumed. It was noticed in calibrating all of the tubes, that, in general, the forward meniscus was larger than the rear one. This seemed to be independent of the direction in which the mercury was moved past a given point and therefore was caused by friction between the wall of the tube and the mercury.

The calibration measurements were made on a Société Genevoise dividing engine. A comparison of the screw with the standard decimeter scale at the Ryerson Physical Laboratory showed only deviations which were well within the limits of experimental error.

A column, about 1.5 cm. long, of triple distilled mercury, which showed no surface impurities, was used as the calibrating thread. The mercury was pushed from one end of the tube to the other, care being taken to see that each new position slightly overlapped a part of the previously measured portion. This insured that all of the tube was covered in the calibration. The column was then forced back and forth a second and third time and its length measured in positions at such distances apart that finally every portion of the tube was covered a second time.

All weighings were made on a chemical balance with the use of a set of Sartorius double check weights accurate to .01 mg. The ordinary precautions for accurate weighing, as double weighing, reduction to weight in vacuo, etc., were observed. It was estimated that the error made in weighing the mercury column for tube No. 2, the smallest tube, was not more than .1 mg. This is an accuracy of 1 part in 7,000 and affects the value of η only .03 per cent. The errors made in the weights of the mercury column for the other tubes were of the same order.

§ 4. THE METHOD.

The simple form of Poiseuille's law is:

$$\eta = \frac{\pi R^4 (p_1^2 - p_2^2) t}{16 V L p_2}.$$

If we substitute in this equation the value of R^4/L obtained from (3) and then, for brevity, use the single letter K to denote

$$K = \frac{U^2 \rho g}{16\pi \int_0^L \lambda^2 dl \left[\int_{l_1}^{l_2} \frac{dl}{\lambda} \right]^2}, \tag{4}$$

ρ being the density of mercury at 0° C. and g the acceleration of gravity, it becomes

$$\eta = \frac{K(p_1 - p_2)(p_1 + p_2)t}{p_2 V}. \tag{5}$$

K, defined by equation (4), is a constant whose value depends on the dimensions of the capillary used. The values of this constant for each tube are given in the last column of Table III. The calibration of the tubes was made at temperatures between 23° C. and 24° C. and reduced to 26° C. by the formulæ[1] used by Fisher in the calibration of his tubes.

TABLE III.

The Dimensions of the Tubes and the Values of Log K.

Tube No.	Length in Cm.	Diameter in Cm.	Log K.
1	99.6062	.046704	$\bar{6}.892782$
2	99.5837	.025843	$\bar{7}.865840$
4*a*	87.4652	.050024	$\bar{5}.069050$
4*b*	77.2469	.050086	$\bar{5}.124663$
4*c*	67.1552	.050156	$\bar{5}.187887$
4*d*	56.9004	.050225	$\bar{5}.262221$
4*e*	51.9656	.050222	$\bar{5}.301507$
5	76.3662	.034228	$\bar{6}.468550$

Equation (5) when corrected for slip becomes

$$\eta = K \frac{(p_1 - p_2)(p_1 + p_2)t}{p_2 V} \left(1 + 4\frac{\xi}{R} \right). \tag{6}$$

The coefficient of slip, ξ, used, is .000083 cm. at a pressure of 76 cm. This is the result obtained by Millikan in his work on the elementary electric charge and is close to that obtained by Warburg[2] by the flow of air through capillary tubes.

If in equation (6), p_1 is the barometric pressure and p_1 and p_2 are large in comparison to their difference, the accuracy of the experiment depends mostly on the measurement of $(p_1 - p_2)$. The apparatus was planned to secure accuracy in the volume of air transpired and both constancy and accuracy in the driving pressure. Transformer oil, in preference to mercury, was used in the manometer and in the apparatus to secure

[1] Fisher, PHYS. REV., Vol. 28, p. 73, 1909.

[2] Warburg, Pogg. Annalen der Physik., Vol. 159, p. 399, 1876.

the difference in pressure, because, it being less dense, lower driving pressures could be read more accurately and the manometer variations were made more noticeable and were more easily controlled. Obermayer and Schneebli used water to secure their pressure difference. Their results show that evaporation introduced an error. The transformer oil having an inappreciable vapor tension eliminated it.

The air used in the experiment was taken from the pressure system in the laboratory and made dust-free and dry by passing it in succession through sulphuric acid, calcium chloride, phosphorous pentoxide and glass wool. Atmospheric pressure at the inlet end of the capillary was secured by the trap *A* (see Fig. 2). This was arranged so that the air

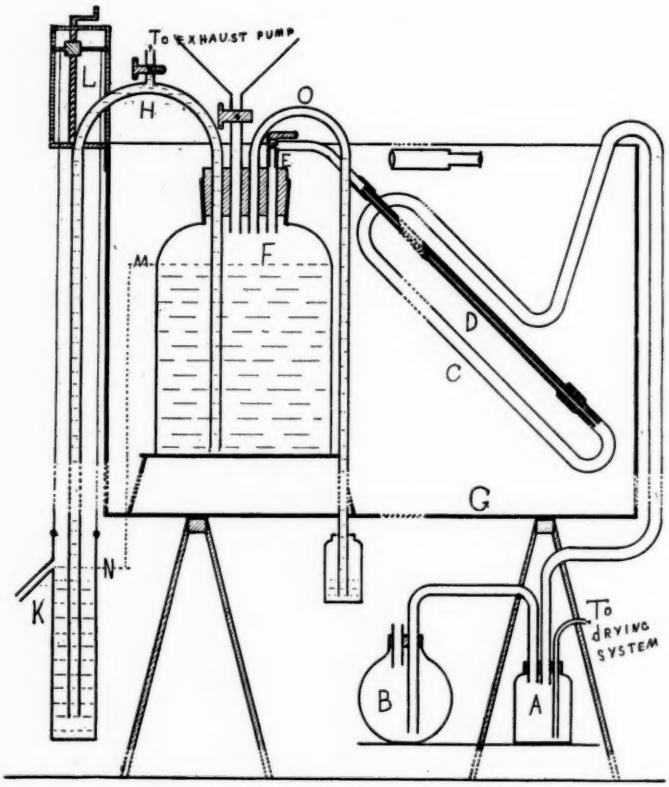

Fig. 2.

which entered from the drying system could pass either into the coil *C* or escape into the atmosphere through a carboy *B*. A layer of phosphorous pentoxide was placed in the latter to provide against the diffusion of moisture from *B* into *A*. The pressure in the trap thus automatically

adjusted itself to that of the atmosphere. The coil *C*, used to insure a constant temperature of the air, was placed between the trap and the capillary *D*. The tubing used in the trap and in the coil *C* was of such size that actual tests showed no fall of pressure along it. From the capillary, the air passed through the stopcock, *E*, into the apparatus for securing the reduction of pressure and the measurement of the volume of air transpired. The coil *C*, the capillary *D*, and the apparatus *F* for measuring volume were submerged in a tank of water *G*. A series of incandescent lamps submerged in the water and lighted automatically by means of a mercury thermostat, kept the temperature at 26° C. with a possible error of .02° C. and with a variation, during the taking of a set of readings, of not more than .003° C. The temperature was measured on a Baudin thermometer of which the tables for reduction to the temperature on the hydrogen thermometer were known. A Beckmann thermometer, graduated in .01° C., was used to determine the constancy of the bath and was compared with the Baudin thermometer at frequent intervals.

The driving pressure was obtained by means of a tube *H*, which led from the bottom of the reservoir *F*, and whose lower end extended into a bucket *K*, which was suspended from a micrometer *L*. When the three were filled with the oil, the air in *F* was under a pressure lower than atmospheric pressure by the weight of a column of oil whose height is the distance *MN* between the surfaces in the reservoir and in the bucket. This height, which is the driving pressure, was not measured directly but by means of the manometer *O*. As the capillary admitted air to the reservoir the pressure in it was kept constant by lowering the bucket with the micrometer at such a rate that the upper surface of the liquid in the manometer was kept stationary. The motion of the image of a lamp, seen in the meniscus, when viewed through a twenty-power telescope, made it easy to control the variation in pressure. The error in maintaining the manometer height constant was absolutely negligible, as the variation in position of the spot of light was not more than .5 mm. from the cross-hairs in the telescope. A variation of .5 mm. in 100 cm., the lowest approximate manometer reading used, shows the accuracy with which the driving pressure was kept constant.

The manometer and outlet tubes were exposed to the room, which could not be kept at a constant temperature. This caused changes in the driving pressure and in the mass of oil in the outlet tube and bucket. The temperature of the manometer was taken as the mean of the readings of two or more thermometers suspended at different points beside it. An error of 1° C. in the temperature of the manometer would cause an error in the result of nearly .1 per cent.

When air enters the reservoir through the capillary, oil is displaced. The volume which flows out of the bucket in a given time is determined from the mass and density. This, when the few slight corrections which follow are made, is the volume of air, V, which has passed through the capillary during the measured time.

A change in the barometric pressure during a test causes a change in the initial volume of air in the reservoir. To make this correction, the approximate volume and the pressure both at the beginning and at the end were determined. The application of Boyle's law gave the correction.

The error caused by the change in temperature in the outlet tube and bucket was estimated from the temperatures and volumes of the oil in the bucket and outlet tube at the beginning and at the end of the observation. The correction for temperature, in a few trials, reached .5 per cent., but was seldom more than .2 per cent.

During the time of observation, the bucket K was lowered. Since the outlet tube extended beneath the surface of the oil, a volume of oil was added equal to a cylinder whose cross-section is that of the tube and whose length is the distance the bucket was moved. Finally a correction due to the vaporization of the oil and to leakage was necessary in the case of tube No. 2 when the driving pressure was greater than 24 cm. of mercury. Frequent tests at other pressures and with other tubes showed that a correction was unnecessary.

Weighings of the oil, in the determination of the volume of air, were made to the .1 g. A set of accurate analytical weights was used and the correction made for weight in vacuo. The accuracy of the balance was such that double weighing was unnecessary.

A comparison of equation (6) with the description of the apparatus shows that the measurement of $(p_1 - p_2)$, p_2 and V depend on the density of the transformer oil used. Thus, since it enters directly in the determination of two of the quantities and indirectly into the third, the density of the oil is actually a factor in the equation as if it were raised to approximately the five-halves power. This necessitated an accurate determination of its density. At least two different samples of each lot of the oil used were tested at several temperatures between 12° C. and 26° C. The line drawn through the mean position of all of the determinations on a given lot of oil showed a maximum variation of the points from the line of 3 parts in 8,400. This would make a probable error in the value of η of less than .1 per cent.

The times were measured by a stop-watch which was compared at frequent intervals with the standard clock in the Ryerson Laboratory. These comparisons showed that the personal error of manipulation was

not more than .4 sec. on any one reading. Errors of adjustment were allowed for and finally when the watch was more carefully adjusted they were negligible. Just before the taking of a set of readings it was wound and during the observation of time was kept in a horizontal position.

The atmospheric pressure was read on a Fortin barometer having a vernier reading to the thousandths of a centimeter. A comparison with the standard barometer at the U. S. Weather Bureau at Chicago was made when work on the problem was begun. The slight difference in the readings was allowed for in the data.

§ 5. THE CORRECTION FOR THE FALL OF PRESSURE AT THE ENDS OF THE TUBE.

Osborne Reynolds[1] has made a study of the flow of water through capillary tubes and finds that Poiseuille's law breaks down and the flow becomes turbulent when

$$1{,}900 < \frac{2U_m\rho R}{\eta} < 2{,}000.$$

ρ is the density and U_m the mean velocity of the liquid in the tube. W. Ruckes[2] has found that this law is applicable to the flow of air through capillary tubes of various lengths and diameters. It will appear from the results which follow that, in my data, there are appreciable departures from Poiseuille's law. If, then, Reynolds' law holds, the velocity of the air in those tubes should be above the critical velocity. The actual value of the velocity of the gas in tube $4e$, at the greatest driving pressure used, was 1,100 cm. per second, while the critical velocity, or the velocity at which, computed by Reynolds' law, turbulent motion sets in and Poiseuille's law breaks down, should be 6,800 cm., that is, six times as large. This does not prove that, when applied to gases, Reynolds' law is in error as to the point when turbulent motion sets in, but rather it demonstrates that there are departures from Poiseuille's law which take place before turbulent motion begins. These departures are due to the energy in the stream lines at the ends of the tubes.

A modification of Poiseuille's law, which corrects for these end effects has been developed by M. Brillouin.[3] He considers that the flow from the one vessel to the other causes a fall in pressure along the stream lines which are outside of the tube. Some kinetic energy is therefore acquired by the moving fluid and some work is done which is not taken into account in the ordinary development of the law. In applying this idea to a gas,

[1] Osborne Reynolds, Scientific Papers, Vol. II., pp. 51 and 535.

[2] Ruckes, Annalen der Physik, Vol. 25, p. 983, 1908.

[3] Brillouin, Lecons sur la Viscosité des Liquides et des Gas, Vol. 1, p. 133; Vol. 2, p. 37.

he states that "This kinetic energy is that of the emergent jet." From this assumption a modified form of Poiseuille's law is shown to be

$$p_1^2 - p_2^2 = \frac{p}{\rho}\left[\frac{16\eta LM}{\pi R^4\left(1 + \frac{4\xi}{R}\right)} + \frac{2M^2}{\pi^2 R^4}\right].$$

M is the mass of gas transpired per unit of time and ρ, the density at the pressure $\frac{1}{2}(p_1 + p_2)$. The other letters have the same significance as elsewhere in this paper. This formula shows that the correction due to the drop in pressure bears the same ratio to the coefficient of viscosity as M bears to $8\pi\eta L$.

Fisher has criticized[1] this in the following words: "The velocity of the emergent jet is not due wholly, as for a liquid, to the initial pressure; a good share of it is due to work done inside the tube itself, especially if the expansion is isothermal and heat energy has been supplied all along the tube to keep up the temperature." Reasoning from this and from O. E. Meyers' integration of the equations of flow of gases through capillary tubes he develops[2] the following formula for the correction to the entrance pressure:

$$R'T \log_e \frac{p_1}{p_1'} = -\frac{1}{384}\left[\frac{p_1^2 - p_2^2}{\eta p_1 L}\right]^2 [R^4 + 12\xi^2 R^2 + 6\xi R^3].$$

R' is the constant of the gas equation, T, the temperature of the gas on the absolute scale, p_1 the pressure to be used in Poiseuille's law and p_1' the manometer pressure measured in the vessel at the end of the tube. A similar formula with the subscripts 2 gives the correction to the exit end.

My own observations, as will appear in the following tables, have been reduced by means of both Brillouin's and Fisher's formula.

§ 6. THE DATA.

The determination of the coefficient was made at three driving pressures. Table IV. includes the complete data of one trial for each of the driving pressures which were used with each tube. On the average, about 10 trials were made at a driving pressure with each tube. The values of $\eta \times 10^7$ in the last column are computed from the data in the corresponding lines and are not corrected for slip or for end effects.

Table V. gives the mean values of η for all of the trials made with each tube at the given driving pressures when the corrections for slip and for end effects have been made. The number of trials made with a tube at

[1] Fisher, PHYS. REV., Vol. 29, p. 152, 1909.

[2] PHYS. REV., Vol. 32, p. 216, 1911.

the given driving pressure is shown in the last column. The probable error, P, is determined from the formula

$$P = \pm 0.67 \sqrt{\frac{\Sigma d^2}{n(n-1)}},$$

in which Σd^2 represents the sum of the squares of the differences between the separate trials and the mean of the n trials.

TABLE IV.

Data for η. Temperature, 26° C.

Tube No.	p_1+p_2 in Cm. of Hg.	p_2 in Cm. of Hg.	p_1-p_2 in Cm. of Hg.	V in Cm.^{3}	t in Sec.	$\eta \times 10^7$ by Equation (5).
1	142.459	67.946	6.674	817.8	1383.8	1838.7
	138.915	64.357	10.227	567.9	605.7	39.3
2	142.828	68.254	6.320	381.6	7203.8	33.1
	138.699	64.233	10.233	400.2	4518.1	31.7
	124.605	50.045	24.515	519.8	2127.4	36.1
4*a*	142.530	68.018	6.504	602.9	693.6	42.3
	139.497	64.601	10.295	605.2	428.4	44.5
4*b*	142.234	67.907	6.420	588.9	606.0	44.0
	138.425	64.128	10.169	582.7	367.4	44.2
4*c*	142.407	68.001	6.405	477.6	425.3	41.2
	138.978	64.408	10.162	669.7	365.4	44.1
4*d*	141.867	67.800	6.267	1132.3	872.4	48.0
	138.487	64.130	10.227	664.9	306.0	59.1
4*e*	143.057	68.375	6.307	951.0	666.2	51.2
	138.751	64.273	10.205	663.4	279.0	56.7
5	138.786	64.308	10.170	405.5	1151.1	32.6

TABLE V.

Mean Values of η at the Different Driving Pressures.

Tube No.	(p_1-p_2) Cm. of Hg. (Approx. Value).	$\eta \times 10^7$ by Equation (5).	$\eta \times 10^7$ Corrected for Slip by Equation (6).	$\eta \times 10^7$ Corrected for Slip and for End Effects.		P, Probable Error $\times 10^7$.	n, Number of Trials.
				By Brillouin's Formula.	By Fisher's Formula.		
1	6 +	1,838.0	1,841.7	1,839.2	1,839.2	±0.5	12
	10 +	1,839.0	1,842.1	1,838.3	1,837.5	±0.3	24
2	6 +	1,833.0	1,838.1	1,837.9	1,837.5	±0.1	2
	10 +	1,831.2	1,836.5	1,836.1	1,836.5	±1.0	4
	24 +	1,834.7	1,840.5	1,839.7	1,839.2	±0.1	3
4*a*	6 +	1,842.1	1,844.7	1,839.6	1,836.6	±0.3	12
	10 +	1,844.4	1,847.1	1,840.1	1,838.4	±0.2	21
4*b*	6 +	1,844.3	1,846.9	1,841.6	1,839.3	±0.2	6
	10 +	1,844.4	1,847.1	1,839.9	1,837.1	±0.2	9
5	10 +	1,832.8	1,836.8	1,834.8	1,834.9	±0.5	16

Table VI. is a condensation of Table V. and gives, in column No. 2, the mean value for each tube when the same weight is given to each trial. In this column the correction has been made for slip. Column No. 3 gives the results in column No. 2 when corrected for end effects by Brillouin's formula and column No. 4 the same results corrected by Fisher's formula.

TABLE VI.

Mean Values of $\eta \times 10^7$ for Each Tube.

Tube No.	$\eta \times 10^7$ Corrected for Slip by Equation (6).	$\eta \times 10^7$ Corrected for Slip and for End Effects.	
		By Brillouin's Formula.	By Fisher's Formula.
1	1,842.0	1,838.6	1,838.1
2	1,838.3	1,837.7	1,837.6
4*a* and 4*b*	1,846.5	1,840.1	1,837.8
5	1,836.8	1,834.8	1,834.9
Mean...	1,840.3	1,837.8	1,837.1

Table VII. shows the final mean values given by three more tubes, 4*c*, 4*d* and 4*e*, which were obtained by cutting off tube No. 4. The corrections for slip and for end effects have been made.

TABLE VII.

Mean Values of $\eta \times 10^7$ for Tubes 4c, 4d and 4e.

Tube No.	Length of Tube in Cm.	$p_1 - p_2$ in Cm. of Hg. (Approx. Value).	$\eta \times 10^7$ by Equation (5).	$\eta \times 10^7$ Corrected for Slip by Equation (6).	$\eta \times 10^7$ Corrected for Slip and for End Effects by		No. of Trials.
					Brillouin's Formula.	Fisher's Formula.	
4*c*	67.16	6 +	1,840.6	1,843.2	1,835.8	1,834.9	4
		10 +	1,844.8	1,847.5	1,838.2	1,832.2	2
4*d*	56.90	6 +	1,850.1	1,852.7	1,842.8	1,839.7	3
		10 +	1,859.5	1,862.2	1,845.9	1,841.7	4
4*e*	51.97	6 +	1,849.5	1,852.1	1,840.0	1,835.9	2
		10 +	1,856.7	1,859.4	1,839.8	1,835.3	4
			Mean.....		1,840.3	1,836.6	

§ 7. A DISCUSSION OF THE DATA.

An analysis of Table V. shows that when the correction for slip alone has been made, different values of η are given by different driving pressures and the same tube, or by different tubes and the same driving pressure. When, however, the corrections are made either by Brillouin's or by Fisher's formula the values are all brought into fairly good agreement. The variations due to a change in the driving pressure alone are

so small, that, from this table, no inference can be drawn as to which method of correction is the better.

But if we compare the values for each tube as found in Table VI., where, with a given tube, each trial receives the same weight, a different result appears. Fisher's formula gives values for three of the tubes which are identical for four figures while Brillouin's correction permits a variation in the fourth place. Too much weight, however, must not be given to this fact, since, if the accuracy of the experiment were what these three results suggest, the values of η obtained at the different pressures for a given tube (see Table V.) would be just as close as the values in Table VI. As this is not the case, Fisher's formula cannot be said to be demonstrated to be better than the other. Table VII., however, contains data favorable to Fisher's formula.

Tube No. 4 was the largest one used and, as is seen from Table V., requires the largest end corrections. To obtain an empirical formula for this correction the tube was shortened by 5 cm. and 10 cm. at a time and the values of η observed and computed.

The original tube, 4*a*, and the second length, 4*b*, gave practically identical results (see Table V.) but the third length, 4*c*, gave values of η which began to differ appreciably with the change in driving pressure (see Table VII.). A comparison of these values at the different pressures for the same length of tube, when corrected for end effects, shows that Fisher's formula makes the variation in the results less than does Brillouin's. Further, the mean of all of the trials is nearer the mean value, given in Table VI., than is the corresponding value obtained by applying Brillouin's expression.

A further careful study of the data in Tables V. and VII. shows that the correction for the end effects is a direct function of the driving pressure and of the fourth power of the radius and an inverse function of the length. This may be expressed by the equation

$$\eta = \eta' \left[1 + \frac{A(p_1 - p_2)R^4}{L} \right]$$

if the terms of order higher than the first are neglected. In this equation A is a constant and η' is the coefficient when corrected for slip. The value of A, determined from the data of tube No. 4, is

$$A = -1.25(10^5).$$

An empirical formula, which will correct the error in η' due to the end effects, is therefore given by

$$\eta = \eta_1' \left[1 - 1.25(10^5) \frac{R^4(p_1 - p_2)}{L} \right].$$

This equation is equivalent to Fisher's correction, as it gives values which are identical within the limit of experimental error with those obtained by his theoretical formula.

The results given in Table VII. are not of such accuracy that one may say that either the empirical or Fisher's formula completely expresses the end effects. The values of η should increase consistently with a decrease in the length of the tube. This they fail to do. The empirical determination of the proper correction for the fall in pressure at the ends of the tube would therefore necessitate a series of more accurate experiments than those on which I have based my absolute determination of η.

§ 8. THE RESULT.

The mean values of η when the different corrections have been made are given in Table VI. Only the data obtained by the use of those tubes in which the end correction is small, have been used for the absolute value of the coefficient. The mean value given by these tubes, when the correction for slip is made, is $1840.3(10^{-7})$. When the correction both for slip and for the end effects are made by Brillouin's formula, it is $1837.8(10^{-7})$ and when made by Fisher's formula, $1837.1(10^{-7})$. The end effects are therefore small but not negligible. Since the two methods of correction give values which differ by but one fortieth of one per cent. their mean is taken as the result obtained in the investigation. This gives an absolute value of $1837.5(10^7)$ g./cm. sec. for the coefficient of viscosity of dry air at 26° C.

The uncertainty in this value of η may be estimated from the following considerations. The maximum variation of a single trial from the mean of the values for a given tube at a given driving pressure is .1 per cent. for the most consistent series and .4 per cent. for the least consistent. The probable error in a given series, as is seen in Table V., is in no case greater than .06 per cent. Such a series of course involves systematic errors which, however, disappear in the mean result found in Table VI., since this table contains completely independent determinations on different tubes. The probable error, in the mean of Table VI., when computed in the usual way, is .04 per cent. This assumes that the correction for the end effects has been properly made. In order to make allowance for possible uncertainties arising from the method of making this correction we may take the total uncertainty in the final value as about .1 per cent. The results found by other observers who have not made

allowance for the variation in the radius are higher than this, as they should be.

The value obtained by Grindley and Gibson is identical, while that given by Fisher differs only by about .1 per cent. My result agrees within .1 per cent. with the mean of the very accurate determinations made by Gilchrist,[1] by the use of a constant deflection method, by Hogg,[2] from the damping of oscillating cylinders, and by Tomlinson,[3] by the damping of a vibrating pendulum.[4] In fact the only careful determinations by any method which do not agree with this were made at the University of Halle by Schultze, by Tanzler and by others using Schultze's apparatus. The reason for their high values is most probably found in the use of the exceedingly small tubes, which makes the determination of the radius difficult and very uncertain.

§ 9. THE SUMMARY.

In the above study of "The Flow of Air Through Capillary Tubes" a number of tubes of different diameters and of very uniform bore were selected and carefully calibrated. With these tubes, both an experimental study of the fall in pressure at the ends and a determination of the absolute value of the coefficient of viscosity of dry air were made.

The study of the end effects leads to the following conclusions:

I. The method of allowing for the end effects, developed by M. Brillouin, holds only for very small corrections.

II. The method developed by Fisher expresses the result better for the corrections within the range of this investigation.

III. The empirical formula,

$$\eta = \eta' \left[1 - 1.25(10^5) \frac{R^4(p_1 - p_2)}{L} \right],$$

which is deduced from the data, gives results which are equivalent to those obtained by Fisher's method.

The absolute value of the coefficient of viscosity of dry air obtained in this investigation at 26° C., when the corrections for slip and for end effects have been made, is $1837.5(10^7)$ g./cm. sec. with an estimated experimental error of .1 per cent.

[1] Gilchrist, PHYS. REV., Series II., Vol. I., p. 124, 1913.

[2] Hogg, Proceedings of the American Academy, Vol. 40, p. 611, 1905.

[3] Tomlinson, Philosophical Transactions of the Royal Society, Vol. 177, p. 767, 1886.

[4] A summary of these determinations is given by R. A. Millikan, "Ueber den warscheinlichsten Wert des Reibungskoeffizienten der Luft," Annalen der Physik, Vol. 41, p. 759, 1913.

In conclusion, I take this opportunity of thanking those who have very willingly assisted during the progress of the research. I wish, especially, to acknowledge the encouragement and the timely suggestions which Prof. R. A. Millikan has given. The investigation was undertaken at his suggestion and was carried to completion under his supervision.

RYERSON LABORATORY,
THE UNIVERSITY OF CHICAGO,
August, 1913.

THE LONGITUDINAL THERMOMAGNETIC POTENTIAL-DIFFERENCE.

BY ALPHEUS W. SMITH.

IF a plate in which there is a longitudinal flow of heat is brought into a transverse magnetic field so that the lines of force are perpendicular to the plane of the plate, it is found that there is a difference of potential set up between any two points at a given distance apart along the plate. This difference of potential is superposed on the thermoelectromotive force which exists in the plate and may serve to increase or to decrease it. Following the usual practice this effect will be considered positive when the potential-gradient established by the magnetic action is in the same direction as the temperature-gradient along the plate. The coefficient of this effect is given by the equation,

$$e = LH\frac{\partial t}{\partial x}l$$

or approximately

$$L = \frac{e}{H(t_1 - t_2)},$$

where e is the difference of potential in absolute units called forth by the magnetic action; H is the magnetic field in absolute units; and $t_1 - t_2$ is the difference of temperature between the two points on the plate at which the lead wires to the galvanometer are soldered, and l the distance between these points.

Zahn[1] has made observations on the way in which this effect in bismuth depends on the temperature. For a magnetic field of 6,290 absolute units he found L to be 0.134 at 28.7° C. and 0.111 at 24.1° C. From these observations he concludes that this effect in bismuth increases with rising temperature. It seemed desirable to study more fully the influence of temperature on this effect in bismuth.

The bismuth plates to be investigated were cast by pouring the molten bismuth into a lavite mould. These plates were about 3 cm. long, 1.4 cm. wide and 0.2 cm. thick. The apparatus for producing the temperature-gradient in the plates was essentially the same as that used by the author[2] in the study of the transverse thermomagnetic effect in nickel

[1] Ann. der Phys., 14, p. 914 (1904).
[2] PHYS. REV., 33, p. 295 (1911).

and cobalt at different temperatures. For the details of the apparatus reference is made to Fig. 1 of that paper. In the present experiments, however, slots were cut in the ends of the rods which were opposite to each other and into these slots the plates to be investigated were inserted. The plates were then clamped to the copper rods by means of screws. To each end of the plate on its longitudinal axis was clamped a copper-advance thermal junction by means of a screw which pressed the junction firmly against the plate. The copper wires of this junction were connected through a galvanometer to a slide-wire potentiometer by which the thermoelectromotive force between the ends of the plate was compensated. The difference of potential set up by the magnetic field was determined by first measuring the electromotive force between the ends of the plate when there was no magnetic field and then measuring it again when the magnetic field was established. The difference between these two electromotive forces gave the difference of potential called forth by the magnetic field. The observations were then repeated with the magnetic field in the opposite direction. The mean of the potential differences set up by the magnetic field in the two directions was taken as the longitudinal thermomagnetic potential-difference. The magnitude of this difference of potential is not exactly the same for both directions of the magnetic field, because it is impossible to get the copper lead wires exactly on the longitudinal axis of the plate so that the transverse thermomagnetic effect cannot make a contribution to the longitudinal effect. The difference of potential from this transverse thermomagnetic effect increases the longitudinal thermomagnetic potential difference for one direction of the magnetic field and decreases it for the opposite direction of the magnetic field. The mean of the differences of potential observed with the magnetic field in opposite direction eliminates this contribution made by the transverse thermomagnetic effect. The mean of the temperatures at the two ends of the plate was taken as the temperature at which the effect was observed. This procedure is not entirely without objection for the longitudinal thermomagnetic potential-difference is not a linear function of the temperature. Since the difference of temperature between the ends of the plate amounted to only 30° or 40° C. the error introduced by this approximation is not serious. The results of the observations on bismuth are given in Table I. The same observations have been plotted in Fig. 1. It is seen from this curve that this longitudinal effect in bismuth decreases rapidly with rising temperature. The slope of the curve indicates that the effect would vanish at the melting point of bismuth. This result is not in agreeemnt with the observations of Zahn who noted an increase in the effect with rising temperature.

The potential-gradient set up by the magnetic action is in the opposite direction to the temperature-gradient in the plate. According to the usual convention this makes the effect in bismuth negative. The average value of the thermoelectromotive force of this bismuth against copper between 32° C. and 72° C. was 6.26×10^{-5} volts per degree Centigrade difference in temperature. At this temperature a magnetic field of 20,000 C.G.S. units sets up in the plate a longitudinal electromotive force which is equivalent to an increase of about 30 per cent. in the thermoelectromotive force.

TABLE I.

t° C.	L	t° C.	L
34.5°	0.116	117°	0.051
41.7	0.110	148	0.040
50.5	0.104	151	0.035
64	0.094	203	0.021
101	0.066	215	0.015

From the curve in Fig. 1 the value of L at 53° C. is found to be 0.102. This value as well as the other values in Fig. 1 is for a magnetic field of

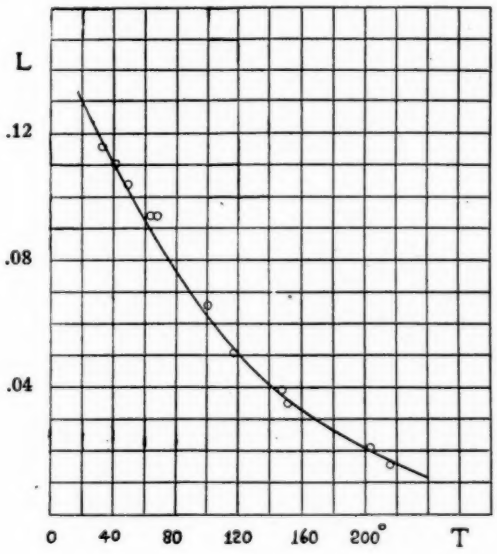

Fig. 1.

9,600 C.G.S. units. For this same temperature and for a magnetic field of 11,000 C.G.S. units Barlow[1] found L to be 0.100,—a value in good

[1] Ann. der Phys., 12, p. 897 (1903).

agreement with that noted above. For a magnetic field of 6,290 C.G.S. units Zahn found L to be 0.111 at 24.1° C. The value of L for this temperature taken from the curve in Fig. 1 is 0.128. Here the agreement is less satisfactory.

Roberts[1] has shown that when graphite is placed in a transverse magnetic field there is a very large change in its electrical resistance. Since the longitudinal thermomagnetic effect is in a way the analogue of the change in the electrical resistance in a magnetic field it seemed that this longitudinal effect in graphite might be large enough to be measured. Two plates of Acheson graphite were made. These plates

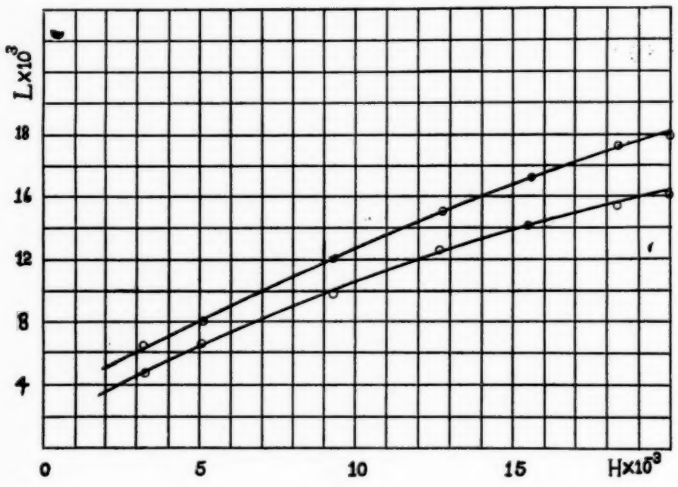

Fig. 2.

were 3.2 cm. long, 1.4 cm. wide and 0.2 cm. thick. The ends were copper-plated and then soldered to copper tubes in the manner described by the author[2] in the study of the Nernst effect in alloys. A description of the apparatus accompanies Fig. 14 of the paper just cited. To the copper-plating on either end of the plate was soldered a copper-advance thermal junction so that the junctions were as nearly as possible on the longitudinal axis of the plate. The temperature-gradient in the plate was established by causing steam at atmospheric pressure to flow through one of the copper tubes and water at room temperature to flow through the other tube. The thermoelectromotive force thus established was compensated on the slide-wire potentiometer when the plate was not in the magnetic field. The potential-difference set up by the magnetic

[1] Phil. Mag. (6), 26, p. 158 (1913).

[2] PHYS. REV., 32, p. 193 (1911).

field was determined by noting the deflections of a d'Arsonval galvanometer. The magnetic field was then reversed and the deflection again noted. The mean of these deflections was taken as a measure of the potential difference set up by the magnetic action. From the figure of merit of the galvanometer the potential-difference was obtained in absolute units. The results of these observations are given in Table II. They have also been plotted in Fig. 2. One end of the plate was at a temperature of about 36° C. and the other end at about 84° C. so that the mean of these temperatures which is 60° C. may be considered the temperature at which the values of the coefficient in Table II. are given. The direction of the effect in graphite is such that the potential-gradient set up by the magnetic field is in the direction of the temperature-gradient in the plate. The effect is therefore positive in graphite. The average thermoelectric height of the graphite against copper between about 36° and 84° C. for Plate I. was 6.17×10^{-6} volts and for Plate II., 5.05×10^{-6} volts. The effect of the magnetic action was to increase somewhat the effective thermoelectromotive force in the plate. The values of L for the two plates differ from each other by about 20 per cent. The reason for this variation is probably to be found in the presence of impurities in the graphite.

TABLE II.

Plate I.		Plate II.	
H	$L \times 10^4$	H	$L \times 10^4$
3,300	65	3,250	48
5,150	80	5,100	67
9,300	121	9,300	98
12,850	151	12,700	126
15,600	173	15,600	142
18,400	193	18,300	155
20,200	197	20,200	160

Table III. contains the data on monel which is an alloy containing 68 per cent. nickel, 29.5 per cent. copper, 1.5 per cent. iron and 1 per cent. manganese. In Curve I. of Fig. 3 the potential difference in absolute units when there is a temperature-gradient of one degree Centigrade per centimeter in the plate, has been plotted against the magnetic field. In Curve II. the coefficient L has been plotted against the magnetic field. The temperature of one end of the plate was 90° C., that of the other end, 24° C. The mean temperature 57° C. may be taken as the temperature at which the values of L recorded in Table III. were determined. The thermoelectric height of monel against copper between

these temperatures is 30.7×10^{-6} volts. In monel the effect is negative so that the potential-difference set up by the magnetic field increases the thermoelectric height of this alloy.

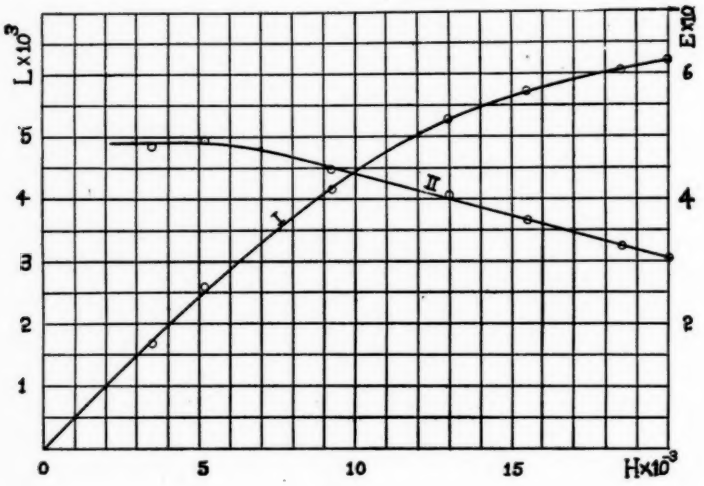

Fig. 3.

TABLE III.

H	$L \times 10^5$	H	$L \times 10^5$
3,500	484	13,000	406
5,200	498	18,500	327
9,300	448	20,000	306

The addition of antimony to bismuth causes the thermoelectric heights to pass through a maximum when the alloy contains about 9 per cent. of antimony. Curve I. of Fig. 4 shows the relation between the thermoelectric height of the alloy and the percentage by weight of antimony in it. In Curve II. of Fig. 4 the coefficient of the longitudinal thermomagnetic potential-difference has been plotted against the percentage by weight of antimony in the alloy. The value of the magnetic field in these observations was 20,200 C.G.S. units. One end of the plate was at about 72° C. and the other end at 22° C. so that the temperature at which the coefficients have been determined is about 46° C. It is seen from this curve that the coefficient of this longitudinal effect has a maximum when the alloy contains about 9 per cent. of antimony. With further addition of antimony to the alloy the coefficient decreases in a manner similar to that in which the thermoelectric heights decrease under

similar condition. The two curves are, however, not parallel. The direction of the effect in these alloys is the same as its direction in bismuth.

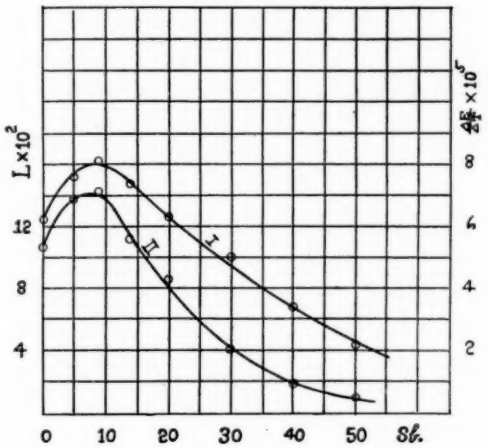

Fig. 4.

SUMMARY.

1. The longitudinal thermomagnetic effect in bismuth decreases with rising temperature and seems to vanish at the melting point of the bismuth.

2. The longitudinal thermomagnetic effect has been determined in graphite and monel. It is positive in the former and negative in the latter.

3. The longitudinal thermomagnetic potential-difference in bismuth-antimony alloys shows a maximum value when the alloy contains about 9 per cent. of antimony.

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THE MEASUREMENT OF MAGNETIC FIELDS BY THEIR DAMPING EFFECT UPON A VIBRATING COIL.

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WHEN a coil of wire which is part of a closed electrical circuit is suspended in a magnetic field and displaced from the equilibrium position, its motion about the axis of suspension will be either periodic and damped, or if the damping is sufficiently great, the coil will approach its position of rest aperiodically. The type of motion is determined by the total resistance in the circuit. If, with a given resistance, it is periodic, the amount of damping will evidently be largely dependent upon the intensity of the magnetic field; and if the motion is to be critically damped, the intensity of the field will again be the factor which determines the resistance of the circuit for this special condition. The dependence of damping upon intensity of field is used as the basis of the work presented in this paper.

I. THEORETICAL.

1. *General.*—The various types of motion which a galvanometer moving coil suspended in the usual way may possess are represented in the general differential equation[1]

$$I_0 \frac{d^2\theta}{dt^2} + 2f \frac{d\theta}{dt} + q^2\theta = 0, \qquad (1)$$

where I_0 is the moment of inertia of the coil about its axis of suspension;

$2f$ is the coefficient[2] of damping;

q^2 is the torsional moment of the suspension fibers per unit angle of displacement;

θ is the angular displacement of the coil at the instant t.

The second term of this equation represents the total damping moment, assuming that damping is directly proportional to the angular velocity of the coil. This assumption is shown by the experimental results of

[1] Love, Theoretical Mechanics, 2d ed., p. 143; Jaeger, Zeitschr. f. Instrumentenk., 23, 1903, p. 262; Diesselhorst, Ann. d. Phys., 9, (4), 1902, p. 459; Ayrton and Mather, Phil. Mag., 46, (5), 1898, p. 377.

[2] "Coefficient," to distinguish this constant from the "damping factor," $\sqrt{\rho}$, used to correct the throws of a ballistic galvanometer for the damping effect.

this paper to be valid. A later derivation[1] shows that the first power variation law holds for that part of the damping moment which is due to the induced currents. The other part of the damping moment is due to viscosity of the air and suspension fibers and to displacement of the air in the path of the moving coil.[2]

The general solution of equation (1) is

$$\theta = \epsilon^{-at}(c_1\epsilon^{\beta t} + c_2\epsilon^{-\beta t}), \tag{2}$$

where

$$a = \frac{f}{I_0} \quad \text{and} \quad \beta = \sqrt{\frac{f^2}{I_0^2} - \frac{q^2}{I_0}}.$$

We shall consider the two cases when β is imaginary and when β is zero. The first condition is fulfilled for $I_0q^2 > f^2$, and therefore implies a value of the damping coefficient less than a certain critical value; *i. e.*, $2f < 2\sqrt{I_0q^2}$. The other condition obtains when $I_0q^2 = f^2$ or when $2f$ has the critical value $2\sqrt{I_0q^2}$. Corresponding to these two conditions are the two types of motion which are most commonly used in the ordinary moving coil galvanometer, namely, damped periodic and critically damped, or "just aperiodic."

2. *Damped Periodic Motion.*—When β is imaginary, equation (2) becomes

$$\theta = \epsilon^{-at}(A \cos bt + B \sin bt), \tag{3}$$

in which

$$b = \sqrt{\frac{q^2}{I_0} - \frac{f^2}{I_0^2}}.$$

Evaluating the constants by imposing the initial conditions which correspond to the discharge of a quantity of electricity Q through the coil at rest—this discharge imparting an initial angular velocity to the coil which is proportional to the quantity discharged, say kQ—equation (3) becomes

$$\theta = \epsilon^{-at}\left(\frac{kQ}{b} \sin bt\right), \tag{4}$$

whence the complete period

$$T = 2\pi\sqrt{\frac{I_0^2}{q^2I_0 - f^2}}. \tag{5}$$

[1] See equation (13), p. 393.

[2] An experiment carried out in connection with this work shows that at diminished pressures, as low as 0.5 mm. of mercury, the logarithmic decrement at any given field value is practically the same as at atmospheric pressure, showing that by far the greater part of air damping is due to viscosity. The effect of viscosity is also proportional to the first power of the linear, and therefore of the angular velocity.

With no damping the complete period is

$$\tau = 2\pi\sqrt{\frac{I_0}{q^2}}. \tag{6}$$

The logarithmic decrement of the motion represented by equation (4) is usually defined as the Naperian logarithm of the ratio of any maximum displacement of the coil to the one next following. Its value is given by

$$\Lambda = \log_e \frac{\theta_n}{\theta_{n+1}} = \frac{a}{b}\pi = \frac{\pi}{\sqrt{\frac{q^2 I_0}{f^2} - 1}}. \tag{7}$$

Designating the angle $(\theta_n + \theta_{n+1})$ by Θ_1 and the angle $(\theta_{n+k} + \theta_{n+k+1})$ by Θ_{k+1}, we have also

$$\Lambda = \frac{1}{k}\log_e \frac{\Theta_1}{\Theta_{k+1}}. \tag{8}$$

By equations (5), (6), and (7)

$$T = \frac{\tau}{\sqrt{1 - \frac{f^2}{q^2 I_0}}} = \tau\sqrt{1 + \frac{\Lambda^2}{\pi^2}}.^{1} \tag{9}$$

The relation between two periods T_1 and T_0 of the same coil corresponding to the two values Λ and λ of the logarithmic decrement is therefore

$$T_1 = T_0\sqrt{\frac{\pi^2 + \Lambda^2}{\pi^2 + \lambda^2}}, \tag{10}$$

which shows that in a given coil a comparatively large change is necessary in the logarithmic decrement in order that the period may be appreciably affected, both Λ^2 and λ^2 being small[2] as compared with π^2.

3. *Critically Damped Motion.*—This case, based upon the condition $I_0 q^2 = f^2$, has been discussed at length by O. M. Stewart.[3] The particular solution of equation (1) is

$$\theta = \epsilon^{-at}(c_1 + c_2 t), \tag{11}$$

which becomes

$$\theta = kQt\epsilon^{-at} \tag{12}$$

by evaluating the constants with the same initial conditions imposed as before.

[1] Bahrdt, Physikalische Messungsmethoden, p. 112; Jaeger, Zeitschr. f. Instrumentenk., 23, 1903, p. 266.

[2] For typical values of Λ and λ see table, p. 398.

[3] Stewart, O. M., PHYS. REV., 16, (1), 1903, p. 158.

II. Equation for Field Intensity—Motion of Coil Periodic and Damped.

Aside from the notation which has already been introduced, the following designations will be used:

H = magnetic field intensity;
l = mean length of coil;
d = mean breadth of coil;
n = number of turns of coil;
T_0 = complete period of coil on open circuit;
T_1 = complete period of coil on closed circuit;
R' and R = total resistance in circuit when motion of coil is periodic, expressed in C.G.S. units and ohms, respectively;
R_0' and R_0 = total resistance in circuit to produce critical damping, expressed in C.G.S. units and ohms, respectively;
M = damping moment due to current induced in vibrating coil;
Λ = logarithmic decrement on closed circuit;
λ = logarithmic decrement on open circuit.

The angle of displacement of the coil is assumed so small that its cosine remains at all times very nearly equal to unity, in order that the coil may cut the lines of force perpendicularly.[1] With this condition imposed, the rate of cutting depends upon only the angular velocity of the coil.

At any instant t when the coil has the angular velocity $d\theta/dt$, the electromotive force induced in the coil is

$$\frac{dN}{dt} = nldH\frac{d\theta}{dt},$$

and if the coil is part of a circuit of resistance R', the current will be

$$I' = \frac{nldH}{R'}\frac{d\theta}{dt}.$$

The moment of the force *due only to this induced current*, opposing the motion of the coil, is equal to $nldHI'$, or

$$M = \frac{(nldH)^2}{R'}\frac{d\theta}{dt}. \qquad (13)$$

There are other factors, however, which must be included in the coefficient $2f$ of $d\theta/dt$ in equation (1).

Let m represent that part of $2f$ which is due to these other causes, *i. e.*,

[1] Using telescope and scale for reading the angle of displacement, the scale being placed at a distance of 50 cm., the deflection may become 10 cm. before the cosine of the angle differs from unity by 0.5 per cent.

to eddy currents, resistance and viscosity of the air and internal friction in the suspensions; m is then the coefficient of damping when the coil swings on open circuit. Hence, on open circuit, $f = m/2$; and on closed circuit

$$f = \frac{(nldH)^2}{2R'} + \frac{m}{2}. \tag{14}$$

From equations (5) and (7)

$$f = \frac{2I_0\Lambda}{T_1}. \tag{15}$$

When the coil is swinging on open circuit, the coefficient of damping

$$\frac{m}{2} = \frac{2I_0\lambda}{T_0}. \tag{16}$$

By equations (14), (15), and (16), with the aid of (10), we obtain for the intensity of the magnetic field the value

$$H = K\sqrt{\frac{R}{T_0}(\Lambda - \lambda)}, \tag{17}$$

in which

$$K = \frac{2\sqrt{10^9 I_0}}{nld}.$$

III. Equation for Field Intensity—Motion of Coil Critically Damped.

The criterion for "just aperiodic" motion was given in connection with equation (12) as $2f = 2\sqrt{q^2 I_0}$. As in the preceding section, the damping coefficient consists of two parts, one of which may be represented by the quantity m. Both parts of the coefficient are proportional only to the angular velocity of the coil. When the motion is critically damped, therefore, the equation of damping has the form

$$\frac{(nldH)^2}{R_0'} = 2\sqrt{q^2 I_0} - m. \tag{18}$$

$q^2 I_0$ being constant for any type of motion of the coil, its value may be obtained from equations (5) and (7):

$$q^2 I_0 = \frac{4I_0^2(\pi^2 + \lambda^2)}{T_0^2}. \tag{19}$$

This together with equations (16) and (18) gives for the strength of the field:

$$H = K\sqrt{\frac{R_0}{T_0}(\sqrt{\pi^2 + \lambda^2} - \lambda)}. \tag{20}$$

But λ^2 is very small as compared with π^2, hence (20) may be written in the form similar to (17):

$$H = K\sqrt{\frac{R_0}{T_0}(\pi - \lambda)}, \tag{21}$$

the constant K being the same as in (17).

IV. Limiting Value of Logarithmic Decrement.

A comparison of equations (17) and (21), term for term, shows that when the damping has become critical, R is replaced by the limiting value R_0, and Λ by the constant π. That the constant π should represent a logarithmic decrement in an aperiodic motion seems at first sight inconsistent with the definition of logarithmic decrement as usually given; for in this case there is no second displacement beyond the null position. The following consideration will show that by adopting a somewhat different definition for the logarithmic decrement, we may consider π still to be a logarithmic decrement in the above equation.

The ordinary definition of the term as applied to the moving coil is based upon the relative magnitude of two successive displacements from the null position, taken at intervals equal to the time of a half-vibration of the coil, as shown by equation (7). Similarly,[1] we may define the logarithmic decrement of an aperiodic motion as the natural logarithm of the relative magnitude of two successive displacements taken at an interval of time equal to $\tau/2$, the half-period when there is no damping. By equation (12), at the instant T,

$$\theta_T = kQT\epsilon^{-aT};$$

and at the instant $T + \tau/2$,

$$\theta_{T+\tau/2} = kQ\left(T + \frac{\tau}{2}\right)\epsilon^{-a(T+\tau/2)}.$$

The ratio of displacements

$$\frac{\theta_T}{\theta_{T+\tau/2}} = \frac{T}{T + \frac{\tau}{2}}\epsilon^{a\cdot\tau/2} = \frac{T}{T + \frac{\tau}{2}}\epsilon^{\pi}.$$

[1] The term "logarithmic decement" has already been applied to a non-periodic velocity (Daniell, Principles of Physics, 1911, p. 185)—a moving body, encountering a resistance which is proportional to the velocity, being negatively accelerated in such a way that during successive equal intervals of time the natural logarithm of the velocity changes by a constant amount.

As T increases, the coefficient of ϵ^{π} approaches unity, so that for values of T which are large as compared with $\tau/2$, *i. e.*, near the end of the motion, the logarithmic decrement, as defined above, becomes equal to π.

V. Discussion of Equations (17) and (21).

It is not a difficult matter to obtain experimentally the data needed for determining a field intensity. After K has once been determined for a given coil, the measurements involve a determination of time,[1] resistance, and angular displacement. All of these enter into the formula under the radical sign, so that the probable error of the result is only half that of the observations. The constant K may be determined either by direct computation from its factors, each of which is readily obtained; or the coil may be suspended in a field of known value and the constant calculated from the observations by means of equation (17).[2] The latter method is used when the number of turns of the coil or its dimensions are not readily obtainable; incidentally, with the dimensions known, the number of turns may be calculated from this determination.

The logarithmic decrements are found by means of equation (8). The error of observation may be reduced to a minimum by taking k sufficiently large; intermediate values of the angle need not be taken, except as a means of checking the result when this is desirable. It is a well-known fact that the logarithmic decrement varies slightly with the amplitude of vibration;[3] but if the displacements are not too large, *i. e.*, approximately not greater than 10 cm. on the scale at a distance of 50 cm., the error is negligible, as shown by the experimental verification of the equations.

From theoretical considerations alone, it would seem preferable to use the periodic method of equation (17) rather than the aperiodic method of equation (21). In the first place, the aperiodic method cannot be used at all for the measurements of fields, the intensity of which is less than that for which the coil is critically damped on short circuit. Again, the observations for equation (21) are more difficult to make than those for equation (17), since it is necessary to adjust a resistance in the coil circuit to such a value that the coil returns to zero in the minimum time without passing beyond. It is difficult to judge exactly when this

[1] The determination of the period of the coil in every measurement of field strength is necessitated by the magnetic impurities in the coil (White, PHYS. REV., 23, (1), 1906, p. 382; A. Zeleny, PHYS. REV., 23, (1), 1906, p. 399; 32, (1), 1911, p. 297; Diesselhorst, Zeitschr. f. Instrumentenk., 31, 1911, p. 247).

[2] It should be noted that when once the constant is known for any particular coil, this coil may, without redetermining K, be used with any kind of suspension; no term in the expression for K is dependent for its value upon the suspension fiber.

[3] Peirce, B. O., Proc. Am. Acad., 44, 1908, p. 72.

condition obtains. The resistance used in (17) is chosen arbitrarily, and may have any value so long as the damping is not too great to make the corresponding logarithmic decrement difficult to obtain.

Experimental tests of the two equations also show the periodic method preferable to the other. Results obtained in using equation (21) have been found in a number of sets of observations to range from three to seven per cent. higher than those given by the ballistic method, the difference increasing with the field strength; as will be seen later, results of the periodic method agree to within one per cent. in almost every case. It is purposed to make a further study of equation (21) to ascertain, if possible, the reason for the observed discrepancy.

There are obviously several advantages of the damped coil method over the ballistic method, principal among which is the simplicity of the apparatus necessary for the determinations. Another is its adaptability to the measurement of a galvanometer field containing an iron core,[1] since the coil will swing as readily about the core as in a free space; furthermore, in a galvanometer field the assumption originally made, namely, that at any instant the coil cuts the lines of force perpendicularly, is more nearly fulfilled than in parallel fields.

VI. EXPERIMENTAL.

To test the accuracy of the method given above, the values obtained by its use for a series of magnetic fields were compared with determinations of the same fields by the ballistic method.

For the purpose of obtaining a variable field of known intensity, an electromagnet with large plane pole pieces was used. The field intensity corresponding to any given current in the electromagnet was first measured by the ballistic method with a test coil of about 10 sq. cm. area having 30 turns. The coil was placed between the poles of the electromagnet, and by means of a rubber band quickly rotated through a half revolution when a release was operated. Throws from the test coil were compared with throws from a standard mutual inductance coil,[2] the coefficient of which had been accurately determined. The primary current in the comparison coil was measured by means of a standard resistance and potentiometer. In order to obtain a definite strength of field with any given current the magnet was, at the beginning of any determination,

[1] A similar method of obtaining H in galvanometer fields has been suggested by White (PHYS. REV., 23, 1906, pp. 390–392), who gives an equation for such a determination. Some of the quantities entering into the equation are, however, difficult to obtain or to estimate with certainty. According to White, the error arising from the use of his formula "seldom exceeds ten per cent."

[2] Zeleny, A., PHYS. REV., 23, 1906, p. 411.

subjected to several cycles of hysteresis, after which the current was increased. The demagnetizing current necessary to overcome the coercive force of the iron was accurately determined, so that zero field could be obtained at will. The magnetization curve was carefully drawn to a large scale, and from it were taken the field values with which the results of the damped coil method were compared.

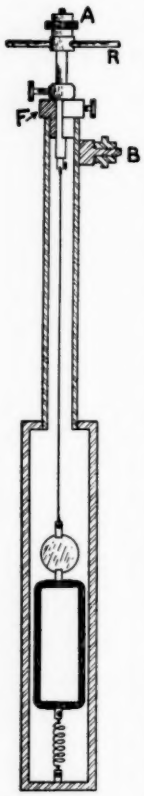


Fig. 1.

For the measurements of field intensities by the damped coil method the arrangement shown in the figure was used. This consists simply of a brass box for supporting a d'Arsonval galvanometer coil (Leeds and Northrup, type H or P) with its upper and lower suspensions. The lower part is square with one side covered with glass, the upper part is tubular. The top post is insulated by the plug *F*, and *A* and *B* are the binding post connectors. The box was supported by a non-magnetic clamp in the space where the magnetic field was to be measured. The galvanometer coil (395 turns, 4.85 × 1.69 cm.) with its suspension had a resistance of 121.7 ohms. The desired displacements of the coil were obtained by sending through it one or more discharges of a ½ mf. condenser charged by a cell. The coil could, by means of a double-throw switch, be thrown at will into the condenser or resistance circuit. It is essential to have the suspensions free from torsion when the coil is in the null position, which is accomplished by first suspending it from the upper suspension alone.

The readings for logarithmic decrements were obtained by means of a telescope and circular scale of 50 cm. radius, placed at a distance of 50 cm. from the mirror. Periods were measured by means of a rated stopwatch. The moment of inertia of the coil was found by comparing its period with that of an accurately turned brass disk of approximately the same mass, each in turn suspended by means of the same 1.5-mil phosphor bronze fiber. I_0 was found to be 3.20 C.G.S. units, and the factor K, 34.80.

A comparison of the results obtained for a series of fields by the two methods is given in the last two columns of the accompanying table. The other columns give data in connection with the damped coil method. The values given for H, as obtained by this method, are in each case the average of three determinations with different resistances in the circuit. Only one of these resistances and the corresponding value of Λ is given for each field. The three determinations for every field were in agreement to a fraction of one per cent.

Magnetizing Current.	T_0	λ	R	Λ	H (Damped Coil Method).	H (Ballistic Method).
0.0998	7.948	.01102	121.7	.01170	3.404	4.4 (about)
0.1199	7.945	.01101	121.7	.02242	14.54	16.5 (about)
0.1885	7.967	.01128	121.7	.18720	57.0	57.0
0.263	7.974	.01190	621.7	.1277	104.5	105.7
0.332	7.948	.01278	1,122	.1399	147.4	148.5
0.414	7.890	.01413	1,622	.1747	199.8	199.0
0.566	7.478	.01742	3,500	.1708	294.7	295
0.983	6.913	.03060	10,000	.2026	548.5	542
1.421	6.428	.04614	20,000	.2079	780	770
1.854	6.128	.06196	40,000	.1800	966	964
2.350	5.891	.07769	50,000	.2025	1,133	1,143
3.500	5.630	.09800	100,000	.1892	1,400	1,405
4.330	5.503	.10678	100,000	.2129	1,528	1,503

Not considering the first two weakest fields given in the table for which the ballistic method gave only approximate values, it is seen that the results of the two methods are in as good agreement as the accuracy of the ballistic method allows.

VII. SUMMARY.

Briefly, the foregoing paper is a presentation of the following:

1. Derivation of an equation for the intensity of a magnetic field in terms of quantities readily obtainable by observations upon a suspended coil vibrating in the field with damped periodic motion.

2. Derivation of a similar equation, depending upon critical damping; and an application of the term "logarithmic decrement" to critically damped motion of a moving coil.

3. Experimental verification of the equations, showing that the method depending upon damped periodic motion may be applied with an accuracy of at least 1 per cent. to the measurement of fields ranging from a few lines to at least 1,500 lines per cm., using the same coil over the entire range.

PHYSICAL LABORATORY,
THE UNIVERSITY OF MINNESOTA,
October 1, 1913.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SIXTY-EIGHTH MEETING.

A REGULAR meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York, on Saturday, October 18, 1913. Vice-president Merritt presided at the meeting.

At the morning session the following papers were presented:

The Vapor Pressure of Metallic Tungsten. IRVING LANGMUIR.

The Form of the Ionization by Impact Function $a/p = f(x/p)$. BERGEN DAVIS.

Change of State Solid-Liquid at High Pressure. P. W. BRIDGMAN.

Notes on Some Integrating Methods in Alternating Current Testing. FREDERICK BEDELL.

Silvered Quartz Fibers of Low Resistance Obtained by Cathode Spray. HORATIO B. WILLIAMS.

The Critical Ranges $A2$ and $A3$ of Pure Iron. G. K. BURGESS and J. J. CROWE.

A Spectrophotometric Study of the Absorption, Fluorescence and Surface Color of Magnesium-Platinum Cyanide. FRANCES G. WICK.

Examination of the Omnicolore Screen Plate by Means of Microscope and Spectroscope. JOHN B. TAYLOR.

Relativity Theory; General Dynamical Principles. (By title.) RICHARD C. TOLMAN.

The Hall Effect in Liquid and Solid Mercury. W. N. FENNINGER.

Failure of Color Photography by Commercial Screen-Plate Methods for Spectroscopic Records. JOHN B. TAYLOR.

Some Experiments on the Magnetic Field of Two Electromagnets in Rotation. S. J. BARNETT.

(Adjourned at 1:00 P. M. for lunch.)—Afternoon Session.

An Electrolytic Determination of the Ratio of Silver to Iodine and the Value of the Faraday. G. W. VINAL and S. J. BATES.

Effect of Amalgamation on the Contact E.M.F. of Metals. F. J. ROGERS.

Relativity Theory; The Equipartition Law in a System of Particles. (By title.) RICHARD C. TOLMAN.

Condition Involving a Decrease of Primary Current with Increasing Secondary Current. F. J. ROGERS.

The Effect of Space Charge and Residual Gases on the Thermionic Current in a High Vacuum. IRVING LANGMUIR.

It was voted to approve the recommendation of the Council that in the case of the annual meeting, the Washington meeting and the Chicago meeting a local committee be given charge of the program for one half-day session, the appointment of this committee to be made by the president of the Society.

Adjourned at 4:30.

ALFRED D. COLE,
Secretary.

CHANGE OF STATE SOLID-LIQUID AT HIGH PRESSURES.[1]

BY P. W. BRIDGMAN.

THE melting temperature and the difference of volume between liquid and solid has been measured as a function of pressure for the following eleven substances: potassium, sodium, carbon dioxide, chloroform, anilin, nitrobenzol, diphenylamine, benzol, carbon tetra-chloride, orthokresol, and phosphorus. The range of the experiments is from 0° to 200°, and up to 12,000 kgm/cm². The melting curves (melting temperature against pressure) all are concave toward the pressure axis, the curvature becoming less at the higher pressures. The change of volume curves are also all similar to each other, but are different from the melting curves in that they are all convex toward the pressure axis. These two facts, together with Clapeyron's equation, indicate that at still higher pressures we are to expect neither a maximum nor a critical point, but that in all probability the melting curve continues to rise indefinitely.

In addition to the experiments on the transition liquid-solid, new allotropic modifications of the solid were found for four of the substances. Benzol and orthokresol have one new form stable at high pressures, carbon tetra-chloride has two new forms, and there are two new forms of phosphorus, one of which changes reversibly into the ordinary yellow phosphorus under the proper conditions, but the other is obtained from the yellow variety by an irreversible reaction at high pressures and temperatures, and is stable under atmospheric conditions. This new form is in appearance like graphite, and has the density 2.60.

THE JEFFERSON PHYSICAL LABORATORY,
CAMBRIDGE, MASS.

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

SILVERED QUARTZ FIBERS OF LOW RESISTANCE OBTAINED BY CATHODE SPRAY.[1]

BY HORATIO B. WILLIAMS.

LOW resistance quartz fibers suitable for use in the Einthoven galvanometer and similar instruments, are usually prepared by chemical silvering. Such deposits are rough and the amount of silver is high in proportion to the conductivity. Cannegieter has shown that smooth fibers can be produced by deposition of a cathode film, followed by electroplating. By the method here outlined, fibers of low resistance can be obtained by the cathode spray alone, thus diminishing the number of manipulations and avoiding all contact with chemical solutions. The cathode is of pure sheet silver bent to a half cylinder. The fibers are held in the discharge tube on a glass frame to which they are cemented with hot shellac. The tube is several times exhausted to .01 mm. and rinsed with dry electrolytic hydrogen. Discharge is maintained at .01 ampere with voltage from 1,200 to 1,500. Direct current is supplied by two small generators with armatures connected in series and fields separately excited. Much gas seems to be occluded during the discharge and a small stream of hydrogen is allowed to leak in steadily, maintaining the current constant. The time of discharge varies with the thickness of film desired. A fiber 140 mm. long, .002 mm. finished diameter with a resistance of 2,700 ohms was obtained by exposure for three hours. The fibers are microscopically smooth and the coating is very compact, uniform and strongly adherent. A liquid air block between the discharge tube and the other parts of the apparatus insures uniform success, but good results can sometimes be secured without it.

DEPARTMENT OF PHYSIOLOGY,
COLUMBIA UNIVERSITY, NEW YORK.

THE EFFECT OF SPACE CHARGE AND RESIDUAL GASES ON THE THERMIONIC CURRENT IN HIGH VACUUM.[1]

BY IRVING LANGMUIR.

THE mutual repulsion of electrons (space charge) in a space devoid of positive ions limits the current that flows from a hot cathode to a cold anode. For parallel plane electrodes of infinite extent, separated by the distance x, and with a potential difference v between them, the maximum current (per unit area) that can flow if no positive ions are present is

$$i = \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\frac{v^{\frac{3}{2}}}{x^2}.$$

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

For the analogous case of an infinitely long hot wire placed concentrically within a cylindrical anode of radius r, the maximum current per unit length is

$$i = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{v^{\frac{3}{2}}}{r\beta^2},$$

when β varies from 0 to 1, according to the diameter of the wire, but for all wires less than one tenth of the diameter of the anode, β is extremely close to unity.

Experiments show that in a very high vacuum (pressure less than .0001 mm.) and with electrodes which do not give off gas the space charge limitation often prevents the thermionic currents from exceeding a few milliamperes. Pressures of gas as high as .001 mm. with voltages above 40 volts usually lead to the formation of sufficient positive ions to neutralize the effect of space charge.

The presence of low pressures of most gases (.001 mm. or less) greatly decreases the electron emission from tungsten. This effect is especially marked at lower temperatures and tends to disappear at very high temperatures. This results in an increase in the value of b of Richardson's equation produced by practically all gases except the group of inert gases.

The proper conditions for obtaining the normal thermionic current from heated metals are discussed. This electron emission is found to be a true property of the pure metal and is not due to secondary chemical effects. For tungsten the thermionic current varies with the temperature in full accordance with Richardson's equation with the following constants:

$$a = 34 \times 10^6 \text{ amps. per sq. cm.},$$

$$b = 55{,}500.$$

Pure electron currents, of even several tenths of an ampere without any perceptible positive ionization, are thus readily obtained. No disintegration of the cathode occurs under these conditions.

The effect of nitrogen in decreasing the thermionic current depends on the voltage of the anode. In many cases much less current is obtained at high than at lower voltages.

The following theory is in full accord with the observed phenomena: The effect of gases in changing the saturation current is due to the formation of a film of an unstable compound on the surface of the metal. The extent to which the surface is covered depends on the relative rates of formation and of destruction of the film. The film may be formed by direct reaction of the metal with the gas or be produced by the bombardment of the metal by positive ions. The film is destroyed by decomposition, volatilization, or cathodic sputtering (bombardment by positive ions).

Research Laboratory,
General Electric Co.,
Schenectady, N. Y.

NOTES ON SOME INTEGRATING METHODS IN ALTERNATING CURRENT TESTING.[1]

BY FREDERICK BEDELL.

AN alternating current or voltage can be measured by a direct current instrument or galvanometer of the D'Arsonval type if a synchronous commutator is interposed between the circuit and the instrument. The reading of the instrument is the integral of the alternating current for half a period, the limits of the integral being determined by the setting of the brushes on the commutator. The brushes may be shifted so as to shift the half period over which the integral is taken. In this way successive instantaneous values may be found of one quantity the value of which depends upon the integral of the quantity directly measured. For example, if the quantity measured by means of the commutator and galvanometer is the current flowing in a condenser, the successive readings of the galvanometer are proportional to the instantaneous values of the charge q of the condenser, since $q = \int idt$. The integral readings of condenser current for any setting of the brushes gives the instantaneous value of q at the moment of commutation. Since potential v is proportional to q, this gives a method for determining the wave-form of potential. If the potential is taken across the terminals of a non-inductive resistance, the wave-form of current is determined.

This condenser current method for determining wave-form is much more sensitive and has a much wider range than various time-honored point-by-point methods. In this and in other integrating methods[2] variation in commutator resistance may be a source of error which may be reduced by perfecting the apparatus or may be made ineffective by choice of method.

CORNELL UNIVERSITY,
ITHACA, N. Y.

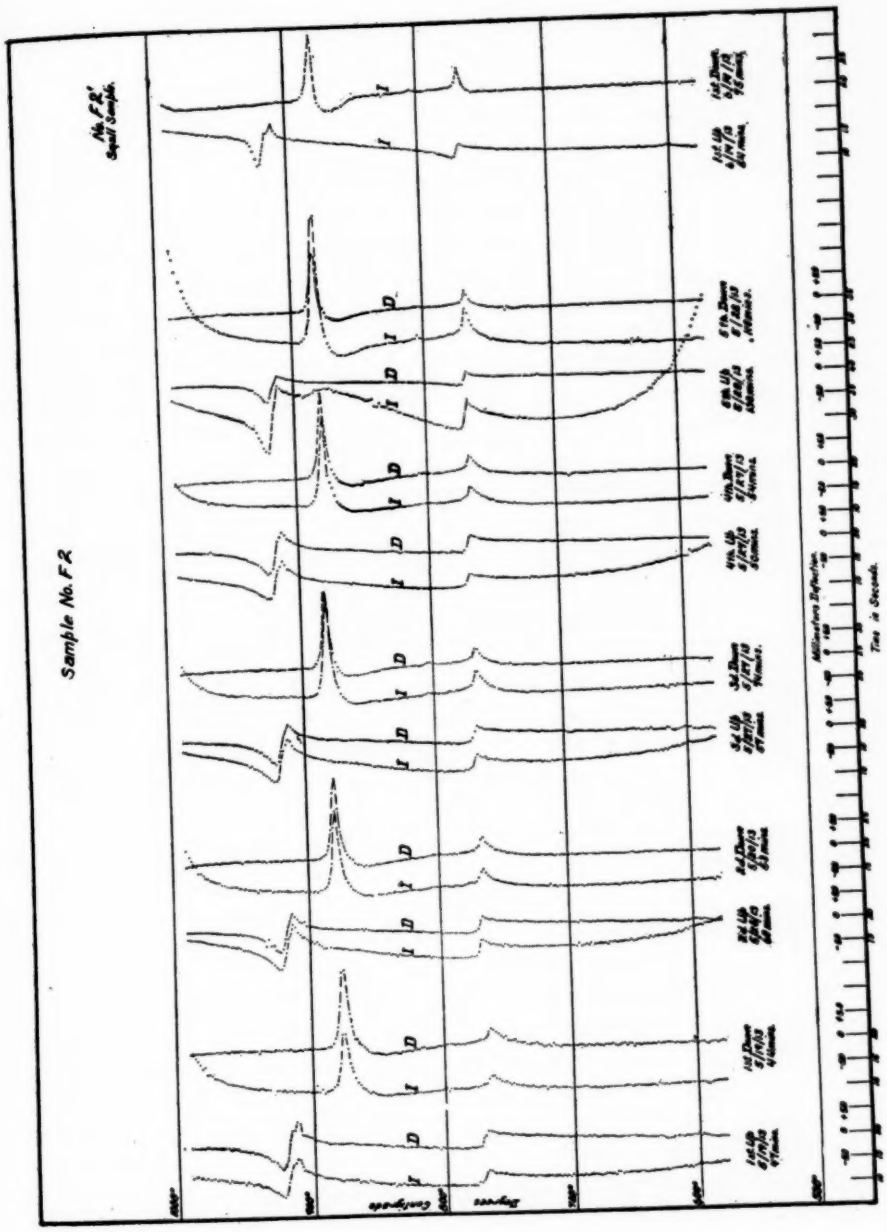
THE CRITICAL RANGES $A2$ AND $A3$ OF PURE IRON.[1]

BY G. K. BURGESS AND J. J. CROWE.

IN spite of a great amount of experimental work and even more theorizing, the question of the allotropy of iron is not yet satisfactorily settled. The separate existence of the lower critical range $A2$ has been seriously questioned by several recent writers; nevertheless all the physical properties of iron which have been studied, with the single notable exception of crystallo-

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

[2] For a detailed description of these methods, see the following papers by F. Bedell: "Condenser Current Method for the Determination of Alternating Wave Form," The Electrical World, August 23, 1913; "The Use of the Synchronous Commutator in Alternating Current Measurements," Journal of the Franklin Institute, October, 1913


Sample No. F 2
No. F 2'
Small Sample.
Time in Seconds.

graphic structure, have shown, in the hands of one or more skillful experimenters, a distinct discontinuity for the lower critical range $A2$ as well as for the upper $A3$ range. For several of the phenomena, such as electrical resistance, thermo-electricity, specific heat, and magnetism, it would appear that the discontinuity is at least as great for $A2$ as for $A3$, while the thermal effect has of course been long recognized as being much the more pronounced at $A3$.

This investigation consisted in taking in vacuo some 130 heating and cooling curves by two methods simultaneously, the inverse rate and differential for 15 samples of pure iron prepared by various methods and analyzed by several chemists. Unusual precautions were taken to secure uniformity of heating of the samples, and it was also possible to take observations for samples of widely different mass and over a wide range of rates each maintained strictly constant. Two furnaces were used and temperatures were taken with six separately calibrated thermocouples. The observations show that in order to get consistent and reliable results in the thermal analysis of a substance such as iron, the properties of which are so readily susceptible to many minor influences, it is necessary to get rid of all the disturbing influences.

We find essential the following precautions:

1. The iron should be pure; our purest samples were 99.983 and contained 0.003 per cent. carbon or less; and it should be kept pure by heating it only in vacuo; a pressure of 0.01 mm. Hg suffices.

2. Either the occluded gases should be removed by premelting the iron, preferably in vacuo, or it will in general be found necessary to take a series of heating and cooling curves at widely different rates, in order to determine correctly the location of the critical ranges $A3$ and $A2$.

3. The iron should be in a single piece entirely surrounding and in contact with the thermocouple junction, otherwise the thermocouple will integrate the irregular progress of the heat through the sample and the curves will lose their sharpness; small samples (1.0 gram or so) give sharper results than large samples.

4. The interval of recording temperatures should be wide enough that sufficient sensibility is attained and narrow enough that the contour of the curves is not distorted; we have found a 2° interval satisfactory.

5. The sensibility of the apparatus indicating temperature and differences of temperature should be of the order of 0.01 degree and time should be measured to better than 0.2 second.

Among the results of this investigation may be mentioned the demonstration that the inverse rate and differential methods, the latter plotted as the derived differential curve, give identical results of the same sensibility for the critical ranges, and the two sets of curves are strictly similar, save for minor particulars.

The plotted curves give what seems to us conclusive evidence of the independent existence of $A3$ and $A2$, all of the 130 curves without exception showing both these critical ranges sharply defined and unquestionably distinct.

It was found impossible to eliminate or attenuate $A2$ by thermal treatment. The $A2$ transformation has not a double cusp, nor do there appear to be other transformations above $A3$ and below $A2$ between 300° and 1050°. With electrolytic iron, unless the sample has been premelted into a compact mass, erratic results will be obtained for both $A3$ and $A2$, the location of the critical points apparently depending in the main upon the rate of heating or cooling. The critical points may even be displaced by over 50°. It is possible, however, to reduce the observations on untreated electrolytic iron to exactly the same temperature basis as the gas-free, compact material by taking curves at several rates and reducing to zero rate. This would appear to indicate that the gases occluded, mainly hydrogen, play no essential chemical rôle in modifying the iron equilibrium.

Even with gas-free iron the $A3$ point is not entirely independent of the rate of heating or cooling, so that it is necessary to reduce the observations to zero rate in order to obtain correct results for $Ac3$ and $Ar3$. The range in the location of $Ar3$, for example, with premelted samples was found to be 876° C. at 0.155 deg./secs. to 897° C. at zero rate.

All preparations of pure iron, even those containing gases, when reduced to the common basis of zero rate of heating or cooling, have the same maximum for the $A2$ critical range, namely, $A2 = Ac2 = Ar2 = 768° \pm 0.5$. All but one of the 15 samples gave this result to within 2°, the other to 3°.

Similarly for zero rate, the value of the maxima of $A3$ are found to be $Ac3 = 909° \pm 1$ and $Ar3 = 898° \pm 2$.

It was not possible to infer a single equilibrium temperature $Ae3$ from these experiments, the $Ac3$ transformation on heating always being at a higher temperature than $Ar3$, the transformation on cooling.

It was found, however, that the beginning of $Ac3$ coincides in temperature with the beginning of $Ar3$ as closely as could be judged. It is as if the crystallographic change at $A3$ required, so to speak, a temperature inertia to complete itself both on heating and on cooling, although the effect of rate on the equilibrium appears to be slightly the greater on cooling.

It is possible that the $A3$ transformation is somewhat more complex than this as there are indications from some of the heating curves of a doubling of $Ac3$ although not of $Ar3$. This effect may be fortuitous.

The relative amounts of heat accompanying the two transformations, $A3$ and $A2$, is approximately $\frac{3}{4}$ to $\frac{1}{4}$ respectively.

An examination of some of the heating curves will perhaps give the erroneous impression that $Ac2$ is an evolution rather than an absorption of heat. The swing back at the maximum is very abrupt following what appears to be a gradual building up of this maximum from an indeterminate low temperature. This behavior would be in accordance with the gradual change in certain physical properties, such as magnetism and electrical resistance, as $A2$ is approached. On the other hand, the operations carried out on sample $F2$ failed to diminish sensibly the intensity of $Ac2$, which would imply that this

thermal transformation is limited to a narrow temperature interval; also some of the curves of $Ac3$ show that this long back swing appears to be in part at least a property of the heating conditions. The shading off on cooling through $Ar2$, if this effect is a real one, might be marked by a similar swing back from this peak, and therefore be indistinguishable.

We hesitate to express an opinion on the nature of the allotropy of iron. The fact that $A2$ appears to be accompanied by no crystallographic change, such as accompanies $A3$ requiring a violent rearranging of relatively large crystal masses and involving a considerable quantity of heat, may account for the sharpness with which $Ac2$ equals $Ar2$, and the $A2$ transformation may be merely molecular not involving the crystallographic structure as such. Whether we have any β iron or not to inhabit the region between $A2$ and $A3$ will depend on our definition of allotropy, but we hope that we have proved beyond a reasonable doubt that under standard conditions there is a definite transformation at 768° and a less well defined although more intense one at 898° to 909° in terms of their maxima on cooling and heating, respectively.

BUREAU OF STANDARDS,
WASHINGTON,
September 2[illegible], 1913.